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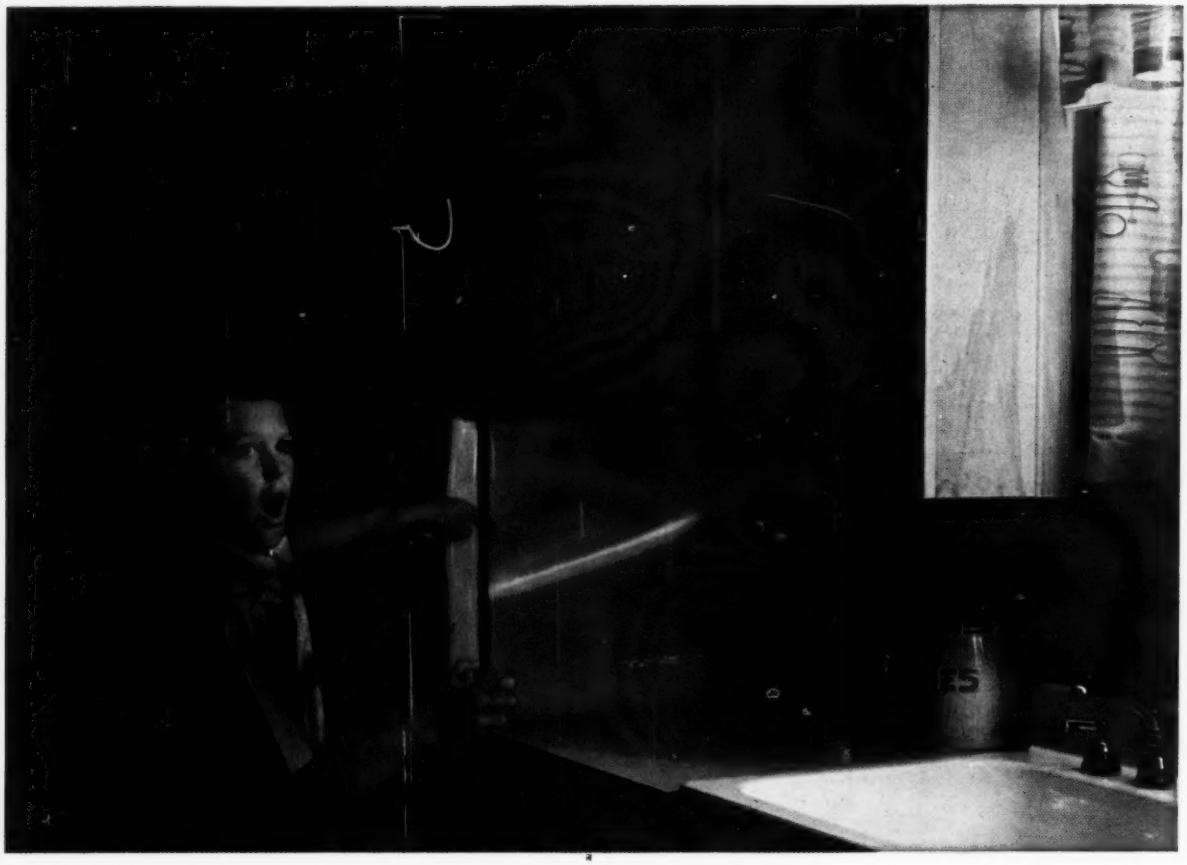

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AMERICAN
DYESTUFF REPORTER
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INTERFACIAL FILM PHENOMENA IN THE DYEING OF CELLULOSE ACETATE

JOHN H SKINKLE* and EDWIN C SHERBURNE**

INTRODUCTION

THE dyeing of cellulose acetate with disperse dyes, being a relatively new process, naturally has been investigated less thoroughly than the dyeing of cellulose or the dyeing of wool; and, consequently, the mechanism of the process is not yet too completely understood. The disperse dyes, which are very insoluble compared with other types, are applied to the fiber from an aqueous dispersion. Theoretical treatment of the acetate dyeing process is made difficult by the complex nature of the dyebath.

According to the solid-solution theory, dyeing occurs only when the dye particles come into contact with the fiber, in which they are highly soluble, forming a solid solution of the dye in the cellulose acetate. Kartaschoff (*3*), a proponent of this theory, believed that the disperse dye particles were completely insoluble in water.

On the other hand, the adsorption theory assumes that the solubility of the dye in water is not negligible. Evidence in support of this belief has been presented by Vickerstaff and Waters (*14*), who showed that very small dye particles actually do exist in the dyebath. This was demonstrated by the fact that a large portion of a dispersion of the dye (1-methylamino-4-anilinoanthraquinone), when placed in a Cellophane bag, was found to be capable of diffusing through the Cellophane and dyeing cellulose acetate, which had been placed in an external solution. Vickerstaff and Waters (*14*) suggested that these smaller particles, which are of near-molecular dimensions and capable of penetrating the interstices of the fiber, actually are responsible for the dyeing, which they consider to take place by adsorption similar in nature to cellulose dyeing with direct dyes. The larger particles then break down as the equilibrium in the dyebath is shifted by the removal of the smaller ones.

Whether the solubility of the dye is negligible or not, the presence of dispersed, solid, dye particles in the dyebath might be expected to cause unusual dyeing behavior; and, in fact, unusual behavior has been observed. In order to determine what action might result when an aqueous dispersion of a substance is brought into contact with an immiscible solvent, Vickerstaff and Waters (*14*) studied the behavior of a dispersion of 1-ethylamino-4-anilinoanthraquinone when shaken with amyl acetate. They found that the amount of dye lost from the dispersion phase was greater than the amount of dye taken up by the solvent; and concluded that the difference was due to a deposition of dye at the interface between the two liquids. In later desorption experiments, these workers (*14*) showed that a similar effect is present in the dyeing of cellulose acetate; but their results showed that the amount of dye in the interface was relatively small. However, both the experiments with the amyl acetate and those with the cellulose acetate were carried out to equilibrium; and it is conceivable that the interface would hold different amounts of dye at times before equilibrium is reached.

This interfacial effect apparently has received little attention; but its importance should not be minimized, since it could be a major factor which will lead to a better understanding of the acetate dyeing process.

This work was performed in an attempt to prove or disprove the existence of a liquid, surface film, having a concentration different from that of the bulk of the dyebath, during the dyeing of cellulose acetate. Provided that such an interfacial film is found to be present, the amount of dye in the film could be determined over the entire dyeing operation until an equilibrium is established between the solution and the fiber.

If a liquid, surface film is present, it should be removed by the rinsing which normally follows the dyeing operation. Also, if this film differs in concentration from the concentration of the main part of the dyebath and if the quantity of dye held at the interface is appreciable, then the amount of dye leaving the solution should differ from the amount of dye taken up by the fiber. Assuming that the amount of dye which has left the solution and the amount of dye actually in the fiber (after rinsing), at a given dyeing time, can be determined accurately, it should be possible to determine the amount of dye in a liquid surface film. If the amount of dye which has left the solution is significantly greater than the amount found in the fiber, a surface film more highly concentrated than the dyebath will be indicated. If the apparent amount of dye lost from the dyebath is less than the total amount of dye in the fiber, then a surface film more dilute than the main dyebath must exist. If the loss from solution is equal to the dye gained by the fiber, either no surface film exists or the method is not sufficiently sensitive to detect a difference. This general line of reasoning was followed in establishing the experimental procedure to be used in this investigation.

It was decided that a series of separate dyeings should be carried out for time intervals ranging from a fraction of a minute up to equilibrium; but otherwise, conditions should be kept the same in all dyeings. It was believed that each dyeing could be stopped, almost instantly, by pouring the contents of the dye beaker into a large volume of ice water at the required time. Sufficient

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dilution of the dyebath should prevent further adsorption of dye; and the rapid cooling should decrease the rate of diffusion enough to prevent any appreciable desorption. The rinse in ice water should also remove a liquid film, if one exists at the fiber surface. By analysis of a sample of the dyebath, collected at the end of the dyeing time, the amount of dye remaining in solution could be determined. The total amount of dye lost from the bath could be calculated by subtracting the quantity remaining in the dyebath from the amount originally present. The amount of dye taken up by the fiber could be determined by analysis of a sample of the dyed fiber. Comparison of the amount of dye lost from the solution with the amount of dye found in the fiber should show whether a liquid, interfacial film is present in the dyeing of cellulose acetate. Similar experiments could also be carried out using an acid dye on wool and a direct cotton dye on viscose rayon, in order to see whether the effect was general or confined to only one type of dyeing.

EXPERIMENTAL

FIBERS——Since the form of the substratum is known to have considerable effect on the overall dyeing rate (7), a basic fiber form was selected for use in all dyeing experiments performed in this work. After being scoured with a nonionic detergent to remove any impurities, acetate yarn, viscose rayon yarn, and wool top were cut with scissors into approximately one-eighth inch lengths so that the fibers would be short enough to prevent excessive tangling or matting during the dyeing. Even with lengths of one eighth of an inch, the fibers would still have lengths in the order of one hundred times their diameters; and the amount of dye entering through the ends of the fibers would probably be insignificant.

It was decided that the dry weight of fiber samples to be used in the dyeing experiments should be one gram. In order to determine the weight of each type of fiber (under atmospheric conditions of 70° F and 65% RH) which would be equivalent to one gram of dry fibers, regain determinations were made in duplicate using the chopped acetate, wool, and viscose fibers after they had come to equilibrium with the conditioning-room atmosphere.

The proper amounts of fibers to give exactly one gram of dry fiber were weighed out, as required for dyeing experiments, on an analytical balance located in the conditioning room.

DYES——In the dyeing of cellulose acetate fibers with a disperse dye, one chief requirement was to use a dye that would be fast to gas fading, since the dyed samples would have to be stored for some time before measurements to determine the amount of dye in the fiber could be made. The disperse dye selected was Eastone Blue BB.

A 100-milliliter dyebath was to be used to dye one gram (dry weight) of fibers (acetate, wool, and viscose); and, consequently, standard stock solutions of the dyes were prepared on this basis.

For the acetate dyeings, a standard dyebath was prepared such that each 100 milliliters of the solution contained 1% of Eastone Blue BB based on one gram of material to be dyed. On an analytical balance, 0.2500 gram of the commercial dye powder was weighed out. The powder was pasted up in a small quantity of hot water, and then diluted to 2500 milliliters by adding cold water. No other additions to the standard dyebath were made, because it was known that some dispersing agent was present in the commercial dye preparation. When examined after standing for five days, the solution appeared perfectly clear. During this period of standing, a thin film of dye had settled out on the bottom of the bottle, but the quantity was believed to be negligible and it was considered doubtful if the stability of the dispersion could be improved upon. Before samples were taken for the dyeings, the bottle was shaken thoroughly to redisperse any particles that had settled. At the same time the standard dyebath was prepared, a one-milliliter sample was taken and five milliliters of acetone were added to get the dye into true solution. The transmission of this solution was measured by means of a photoelectric colorimeter. The transmission of a sample taken 45 days later and treated in the same way showed no significant difference from the transmission of the original sample, indicating that no measurable change in the dyebath had occurred.

The acid dye chosen for the dyeing of wool fibers was Anthraquinone Blue B (old *CI* 1054; new *CI* 63010).

Two and one-half liters of a standard dyebath were prepared, containing 0.2500 gram of the commercial dyestuff, 0.750 gram of acetic acid, and 3.75 grams of anhydrous sodium sulfate. Therefore, each 100 milliliters of the standard dyebath contained 0.01 gram or 1% of the dye, 0.03 gram or 3% acetic acid, and 0.15 gram or 15% sodium sulfate, the percentages being based on a one-gram sample of wool fibers to be dyed.

The dye selected for the dyeing of viscose rayon fibers was Pontamine Sky Blue 6BX Conc 150% (old *CI* 518; new *CI* 24410), a direct cotton dye.

A standard solution of the direct dye was prepared by pasting up 0.2500 gram of the commercial powder in a small volume of hot, distilled water; diluting to about one liter with cold water; adding 3.75 grams of CP, granular sodium chloride which had previously been dissolved in water; and further diluting to a final volume of two and one-half liters by adding cold, distilled water. One hundred milliliters of the standard dye solution were to be used in each dyeing to dye one gram (dry weight) of chopped, viscose fibers; and, therefore, basing percentages on the weight of material to be dyed, the dyebath would contain 1% of the commercial dyestuff and 15% of sodium chloride.

APPARATUS——The dye beaker was constructed especially for this work. It was made with an external jacket, through which water from a constant temperature bath at 60° C could be pumped to keep the dyebath at the required temperature (Figure 1). The beaker was made entirely of Pyrex glass; its capacity was approximately 150 milliliters. A reflux condenser was fitted to the top of the beaker by means of a large rubber stopper covered with aluminum foil, in order to prevent losses from the dyebath by evaporation.

Agitation in the dyebath was supplied by a variable-speed, magnetic-type stirrer. The dye beaker was set directly upon the housing of the stirrer motor. A Teflon-covered, cylindrical bar magnet, having a length slightly less than the inside diameter of the dye beaker, was dropped into the dyebath. Turning on the stirrer motor caused this stirring bar to rotate, and the rate of stirring could be controlled by adjustment of a rheostat knob. The knob was set to give a fairly high rate of stirring, which was kept the same in all dyeings.

In planning the experimental work, it was decided that individual dyeings would be run for the following numbers of minutes: 1/16, 1/4, 1, 4, 9, 16, 25, 36. . . . and so on, up to the length of time necessary to reach equilibrium. The timing of a fairly long dyeing presents no particular problems, but running a dyeing for exactly 1/16 of a minute (3.75 seconds) is quite difficult. In such a short dyeing, an error of one or two seconds in timing represents a considerable part of the total dyeing period. For

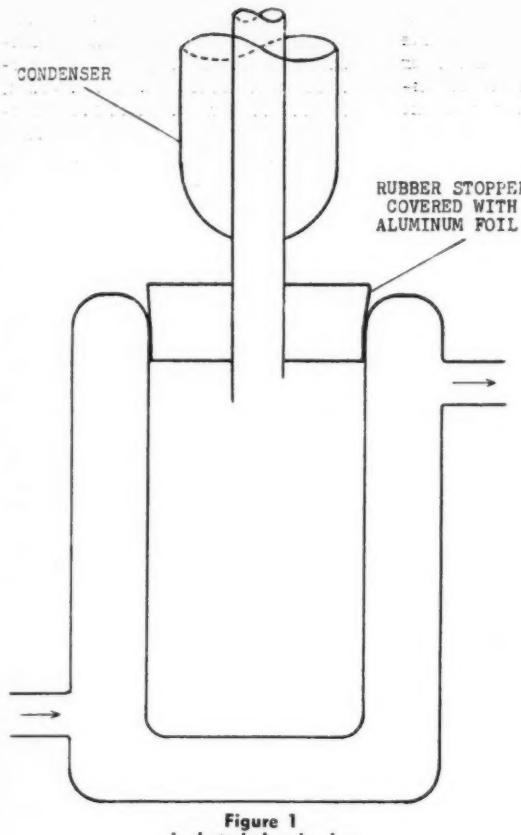

Figure 1
Jacketed dye beaker

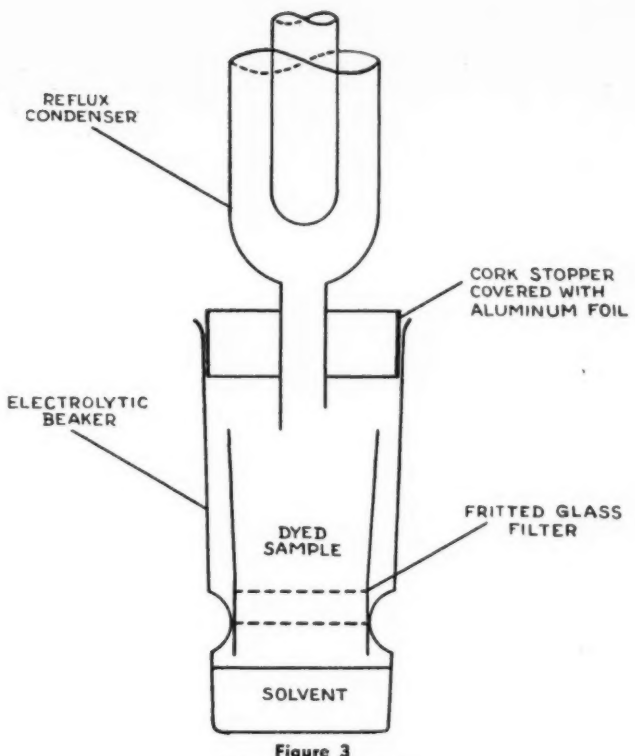

Figure 3
Extraction apparatus

this reason, a special apparatus was constructed so that the short dyeing times would be known more exactly.

As shown in Figure 2, the apparatus consisted of a synchronous-motor, clock timer, which was connected in an electric circuit (110 V, A C) containing a three-amp fuse. The clock circuit was tapped by two wires which were drawn through a length of bent, glass tubing leading into a partially filled beaker of ice water. The bent glass tube was mounted with one end just above the surface of the ice water. The tap wires were made to terminate about one-half inch above the end of the glass tubing, and their ends were stripped of insulation. The end of the glass tubing was sealed, around the wires, with Canada balsam cement. A short length of rubber tubing was fitted over the end of the glass tubing to form a small cup around the bared ends of the wires. The bared wires were bent so that they would be very close together, without quite touching.

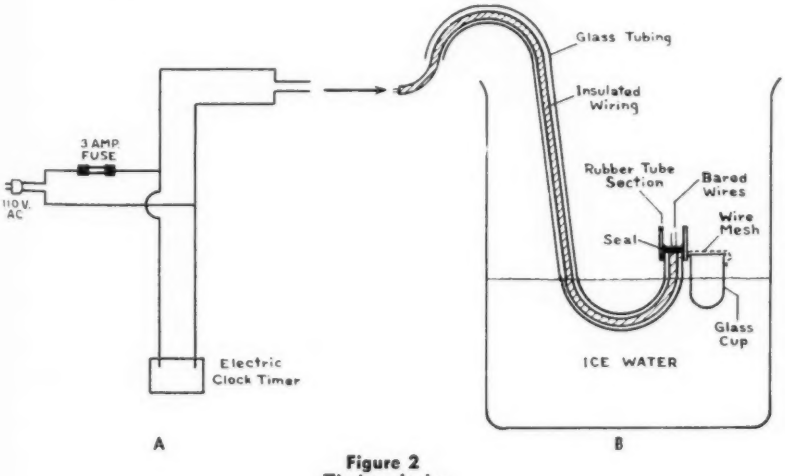

Figure 2
Timing device
A—Circuit diagram
B—Apparatus

The use of the timing device probably can best be explained by going through the procedure used in a typical short-time dyeing. Before the dyeing was started, the rubber tubing around the bared wires was filled about half full of anhydrous sodium sulfate. After all necessary preparations for the dyeing were made, the clock timer was started. At the instant the timer reached a certain, predetermined number of seconds, the dyeing was started by dropping the fiber sample into the dyebath. When the dyeing had run for the required number of seconds, the contents of the dye beaker were quickly poured into the ice water to stop the dyeing. In the pouring, the dyebath was directed so as to strike the bared wires just above the surface of the ice water. Because of the salt present, this caused a short circuit and the clock timer was stopped at the instant the dyebath and fibers entered the ice water. The clock timer could be read to the nearest

tenth of a second; and by subtracting the starting time from the stopping time, the actual time of dyeing could be known quite accurately. It was sometimes necessary to make several attempts before a dyeing time sufficiently close to the one desired could be attained.

In order to determine the amount of dye taken up by samples of wool and viscose rayon, it was decided that a solvent-extraction method using aqueous pyridine solution probably would be best. Aqueous pyridine solutions usually are effective in removing acid dyes from wool and direct dyes from cellulosic fibers. Since no completely satisfactory apparatus could be found for the extractions, the one shown in Figure 3 was designed and constructed. This apparatus consists of a modified, electrolytic beaker, a fritted-glass filter, a cork stopper covered with aluminum foil, and a reflux condenser. Four indentations, equally spaced around the sides, were made in the electrolytic beaker to hold the fritted-glass filter about ¾ of an inch above the bottom of the beaker. The reflux condenser was fitted to the top of the beaker by means of a cork stopper, which was covered with aluminum foil to protect it from the pyridine.

In use, the aqueous pyridine solution was placed in the bottom of the beaker, below the glass filter. A weighed sample of the dyed fiber was placed inside the fritted-glass filter. Heat from a Tirrill burner was applied, and the flame was adjusted to produce a gentle boiling of the pyridine solution. Condensation in the reflux condenser caused the pyridine-water mixture to drip over the dyed fibers, gradually extracting the dye and carrying it through the filter and back into the bottom of the beaker.

This apparatus was found to be very satisfactory, since it required very little attention during its operation, and only about 25 milliliters of the aqueous pyridine solution were needed for each extraction.

GENERAL DYEING PROCEDURE ———The following steps indicate the general dyeing procedure which was used in the dyeing of cellulose acetate, the dyeing of wool, and the dyeing of viscose rayon:

1) The constant temperature bath was turned on and allowed to come to the required temperature of 60° C.

2) Samples of the conditioned fibers, of the proper weight to give exactly one-gram samples of the dry fibers, were weighed out in tared Gooch crucibles on an analytical balance. The sample to be dyed was wet out by pouring distilled water through the crucible several times. The crucible containing the sample was then placed in a beaker containing just enough distilled water to cover the fibers without running over the top of the crucible. The beaker was partially immersed in the water of the constant-temperature bath in order to heat the fiber sample to 60° C.

3) The standard dye solution was shaken thoroughly and 100 milliliters of the solution were transferred (by pipette) to the dye beaker. After the magnetic stirring-bar was introduced and the reflux condenser clamped in place, the pump used to circulate water from the thermostat through the jacket of the dye beaker was started. The magnetic stirrer was also turned on and adjusted to the proper speed, which was kept constant in all the dyeings.

4) After the water in the constant-temperature bath had reached the proper temperature, twenty minutes were allowed for the fiber sample and the dyebath to be heated to 60° C.

5) Just before the dyeing was started, the condenser was lifted from the top of the dye beaker. Excess water was removed from the sample by squeezing the fibers against the side of the Gooch crucible with a spatula. The fiber sample was then lifted on the spatula and held over the open dye beaker.

6) The dyeing was started by dropping the fiber sample into the dyebath and, at the same instant, starting a mechanical clock timer. Then the condenser was replaced to keep the volume of the dyebath constant.

7) Just about a minute before the dyeing was stopped, the condenser was again removed from the top of the dye beaker. At the required time, the dyeing was stopped by quickly pouring the contents of the dye beaker into a large volume of ice water. The ice water was prepared about twenty minutes earlier by placing approximately one liter of distilled water in a two-liter beaker, and adding sufficient ice cubes (prepared with distilled water) to reduce the temperature of the water and maintain it at 0°C. A sample of the dyebath was collected at the instant the dyebath was poured out by means of a small, glass cup, which was covered with a stainless-steel screen (to filter out fibers) and mounted just above the surface of the ice water. This sample was used to determine the amount of dye remaining in the dyebath at the end of the dyeing.

8) The dyed fibers were collected from the ice water by suction-filtration through a Gooch crucible. The fibers were allowed to dry for several hours at room temperature, and the drying was completed by heating in an oven for two hours at 60° C. The dyed samples were transferred immediately from the oven to the conditioning room (in closed containers), where they were exposed to an atmosphere of 70° F and 65% RH.

Individual dyeings were run for lengths of time such that the square roots of the dyeing times in minutes would be ¼, ½, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, . . . etc; and, therefore, the actual dyeing times, in minutes, were 1/16, ¼, 1, 4, 9, 16, 25, 36, 49, 64, 81, 100, . . . etc. The dyeing time was increased, according to this series, until a large increase in dyeing time showed no appreciable change in the measured exhaustion value, indicating that an equilibrium between fiber and solution had been reached.

For the short dyeings (4 minutes and less), a slightly different procedure was used. The bared ends of the wires of the timing device previously described were mounted above the surface of the ice water, as shown in Figure 2. The length of rubber tubing around the bared wires was partially filled with anhydrous sodium sulfate, and the electric clock timer was started. At a predetermined number of seconds on the timer, the fiber sample was dropped into the dyebath to start the dyeing. When the dyebath was poured over the bared wires, and into the water, a short circuit caused the clock timer to stop. The actual time of dyeing was determined by subtracting the starting time from the stopping time. If found to be necessary, the process was repeated until a dyeing for the proper length of time was obtained. The reflux condenser on the dye beaker was removed during these short dyeings, since it was believed that losses by evaporation over a four-minute period would be negligible. The dyebath sample was collected as previously described, and the method of mounting the small, glass cup above the surface of the ice water is shown in Figure 2.

ANALYSIS OF SAMPLES FROM THE DYEING OF CELLULOSE ACETATE———

a) Dye in the Dyebath: A calibration curve was prepared to be used in measuring the concentration of the disperse dye in the dyebath.

Dilutions of the standard dyebath were made with distilled wa-

ter to correspond to dyebath exhaustions of 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100%. (Distilled water alone was used to represent 100% exhaustion). To exactly one milliliter of each of these dilutions, 5 milliliters of CP acetone were added with a pipette to get the dye into true solution. With a Cenco Photoelectric Colorimeter, the transmission of each of these solutions was measured. A calibration curve was prepared by plotting the logarithm of the transmission against the concentration for each solution.

Samples of the dyebath were analyzed by adding 5 milliliters of acetone to one milliliter of the dyebath sample, and measuring the transmission of the resulting solution with the colorimeter. The concentration of dye in the dyebath sample was read from the calibration curve, and the total amount of dye in the dyebath (100 ml) was calculated. By subtracting the total amount of dye in the dyebath from the amount originally present, the amount of dye lost from the bath was determined.

b) Dye in the Fiber: For the determination of dye in the dyed fiber samples, the calibration curve was prepared by dissolving known amounts of dye and undyed acetate fibers in measured volumes of acetone-water mixtures containing 80% acetone and 20% water by volume. (80% acetone was found to dissolve the commercial dyestuff better than CP acetone).

Solutions were prepared containing known amounts of dye dissolved in a total volume of 30.0 milliliters of 80% acetone, and 0.5000 gram (dry weight) of undyed acetate fibers were dissolved in each solution. The solutions contained amounts of dye corresponding to 1.0, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05, and 0% dyeings on one-half gram of fiber. The 0% "dyeing" contained only 0.5000 gram of acetate fibers dissolved in 30 milliliters of 80% acetone, and was used as a blank in the optical measurements to eliminate the effect of dissolved fiber. The transmission of each solution was measured; and the logarithms of the transmission values were plotted against the concentrations of dye per gram of dry fiber.

After being conditioned at 70° F and 65% RH for at least 48 hours, samples of dyed fibers from the acetate dyeings were weighed out on an analytical balance, so that each sample would weigh 0.5000 gram on the dry basis. The samples were transferred to 4-ounce bottles, 30.0 milliliters of 80% acetone were added to each, and the bottles were tightly capped. Each bottle was then shaken until the dyed fiber was completely dissolved; and the transmission of the solution was measured with the colorimeter, which had previously been adjusted so that a blank consisting of one-half gram of undyed fiber (dry basis) in 30.0 milliliters of 80% acetone would have a transmission of 100%. From the calibration curve, the amount of dye per gram of dry fiber was determined for each sample.

ANALYSIS OF SAMPLES FROM THE DYEING OF WOOL AND THE DYEING OF VISCOSE RAYON ———Both the acid dye used in the dyeing of wool and the direct cotton dye used in the dyeing of viscose could be treated in much the same way, since they are both water-soluble dyes. It was also found that both dyes could be extracted from their respective fibers by means of a pyridine-water mixture.

a) Dye in the Dyebath: For both the acid dye and the direct dye, calibration curves for determining the amount of dye remaining in the dyebath were prepared by making dilutions of the standard dyebaths with blank dyebath solutions. The blank dyebath solutions contained the same amounts of all the constituents in the standard dyebaths, except that the dyes were not added. The dilutions were made to produce solutions corresponding to dyebath exhaustions of 0, 20, 40, 60, 80, 90, 95, 97.5, 98.75, and 100% (blank dyebath). To one milliliter of each dilution, 5 milliliters of the blank dyebath were added by pipette; and the transmission of each solution was measured with the colorimeter. The data was used to plot a calibration curve.

One-milliliter samples from the solutions collected at the end of each dyeing were diluted by adding 5 milliliters of blank dyebath solution from a pipette. Transmission measurements were made; and, with the aid of the calibration curve, the amount of dye left in the dyebath and the amount of dye exhausted from the bath were calculated for each dyeing time.

b) Dye in the Fiber: The dyed samples of wool and viscose rayon were subjected to an extraction treatment with aqueous pyridine solution, in order to remove the dye. Dilutions of the extracts were analyzed colorimetrically to determine the amount of dye present. The following procedure was used for each dyed sample:

A sample of the conditioned, dyed fibers, having a weight equivalent to 0.2500 gram of fiber on the dry basis, was weighed out on an analytical balance in a tared, fritted-glass filter. The fritted-glass filter was placed inside the extraction apparatus, as shown in Figure 3. Approximately 25 milliliters of an aqueous pyridine solution containing 25% pyridine by volume were allowed to drain over the fibers from a pipette. Most of this solution passed through the filter and collected in the bottom of the electrolytic beaker. The stopper and condenser were fitted to the top of the beaker, water was circulated through the condenser, and heat was applied to the bottom of the beaker by means of a Tirrill burner. The flame was adjusted to produce gentle boiling of the solvent.

Drops of the condensate, falling on to the sample, gradually extracted the dye and carried it into the bottom of the beaker, where it remained with the bulk of the solvent. When it appeared that all of the dye had been removed, the extraction process was stopped. After the solution containing the extracted dye was allowed to cool to approximately room temperature, it was poured into a 50-milliliter volumetric flask. Small quantities of the 25% aqueous pyridine solution were used to rinse the fiber sample and wash out the extraction apparatus; and the washings were also poured into the volumetric flask, which was filled to the mark by adding more of the aqueous pyridine mixture. The transmission of this final solution was measured with the colorimeter, using 25% aqueous pyridine solution as a blank; and the concentration of the dye in the fiber was determined by means of a calibration curve.

This calibration curve had been prepared previously by measuring the transmissions of 25% aqueous pyridine solutions containing known amounts of dye, and plotting the logarithms of the transmission values against dye concentrations.

RESULTS

In the absence of any interfacial effects, the dye disappearing from solution should represent the dye adsorbed by the fiber; and exhaustion values for the same dyeing time should check (within experimental error) whether determined by solution measurements or by fiber measurements.

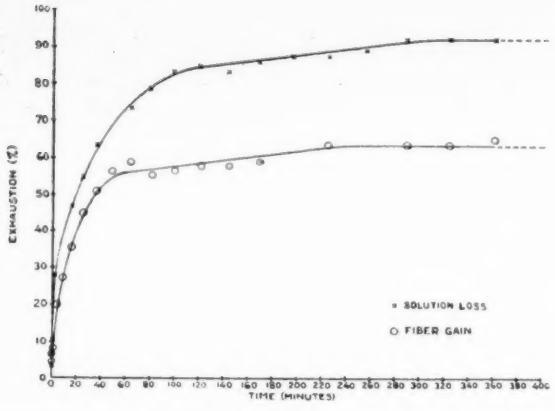

Figure 4
Exhaustion vs time

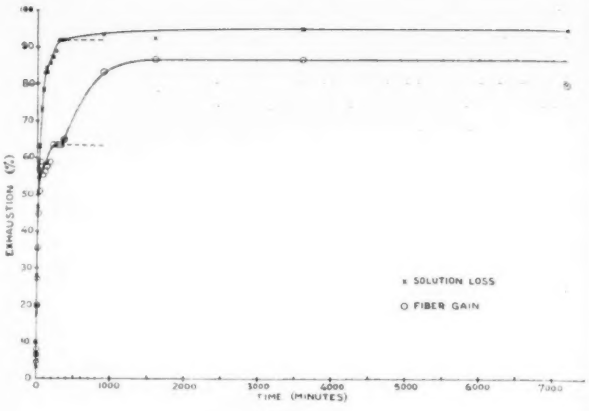

Figure 5
Exhaustion vs time

Actually, however, in the dyeing of cellulose acetate with Eastone Blue BB, a substantial difference was found to exist between the two values; the exhaustion determined by fiber measurements being consistently much lower than that determined by solution measurements. Comparisons can be made by referring to Figure 4, which is a plot of both exhaustion values against the time in minutes for the first six hours of the dyeing. A significant difference is seen to exist between the Solution-Loss curve and the Fiber-Gain curve even after a very few minutes. The difference increases for a time, but then remains quite constant from 80 minutes to 361 minutes. Also, there is a tendency for both curves to level out in the region from 225 minutes to 361 minutes, which was taken originally as an indication that an equilibrium between solution and dyed fiber had been reached. A subsequent dyeing that was run for 900 minutes, however, showed a substantial increase in the amount of dye taken up by the fiber and a slight increase in the amount of dye lost from solution. Therefore, in an attempt to reach a true equilibrium, still longer dyeings were carried out, the longest of which was run for 7200 minutes (5 days). Figure 5 is a plot of exhaustion against time for the entire dyeing curve. Due to the drastic change in the time scale, which was necessary to include all the points on the same graph, the separation between the curves at short time intervals is no longer apparent in Figure 5. However, the difference between curves continues to increase until in one area it amounts to nearly 30% of the dye in the system. Even after 7200 minutes of dyeing, the curves do not come together, but apparently each levels out at its own equilibrium value. Although there is an indication that both curves are leveling out at about 300 minutes, each eventually reaches a true equilibrium, which, in the case of the Fiber-Gain curve, is considerably higher.

After it was determined that errors in the calibration curves, volatilization of the dye, or decomposition of the dye were not responsible for the difference observed, it was believed that the dye lost from solution but which did not turn up in the fiber must be present in a liquid film at the surface of the fiber during the dyeing. A liquid film would explain the difference, since such a film would be removed by the brief, ice-water rinse that was a part of the dyeing procedure.

A repeat dyeing was carried out for 324 minutes, where the difference between solution-loss and fiber-gain was at a maximum, but in this case the rinse in ice water was eliminated. Instead, at the end of the dyeing, the contents of the dye beaker were poured over a stainless-steel, wire screen, which was mounted over a beaker. The dyed fibers were collected on the screen, but the solution passed through the screen and was caught in the beaker. The dyed fibers were allowed to drain for a few seconds; and then the screen (containing the fibers) was placed on top of a second beaker, where as much of the retained dye liquor as possible was squeezed out of the fiber sample and collected in this second beaker. The dyed fibers were dried in an over at 60° C, and conditioned at 70° F and 65% RH.

It was believed that, if a highly concentrated, liquid, surface film was present during the dyeing, three things could occur in this experiment in which the ice-water rinse was eliminated:

1) The film could remain unbroken on the surface of the fiber, in which case the dye in the film would be determined along with the dye actually in the fiber.

2) The film could be completely or partially broken when the contents of the dye beaker were poured out; in which case part of the dye in the film would drain through the screen into the first beaker, part of the dye in the film would be squeezed out and collected in the second beaker, and part of the dye in the film would be retained by the fiber———either in a partially broken film or in dye liquor which could not be removed by squeezing.

3) The film could be completely unbroken when the contents of the dye beaker were poured out, but either completely or partially broken when the sample was squeezed out. In this case, the solution drained out of the sample into the first beaker would have a lower concentration of dye than the solution removed by squeezing, which was caught in the second beaker. It was believed that by analysis of the solution drained out of the sample, the solution squeezed out of the sample, and the dyed sample, it would be possible to account semiquantitatively for all the dye in the system and to learn something about its location, even though the experiment was not designed for the highest accuracy.

Analysis of the solution drained from the sample and analysis of the solution squeezed from the sample showed that the concentration of dye in each was the same; therefore, they were treated as the same solution. The total amount of dye in the dyebath and the total amount of dye

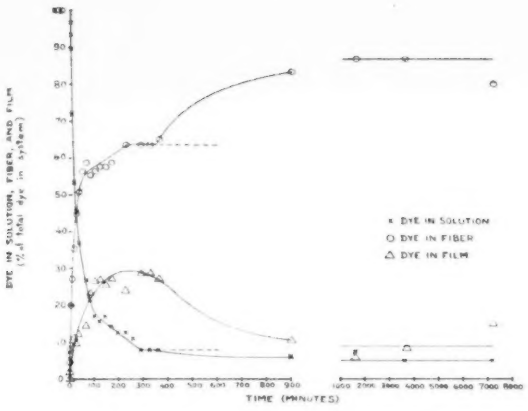

Figure 6
Dye in solution, fiber, and film vs time

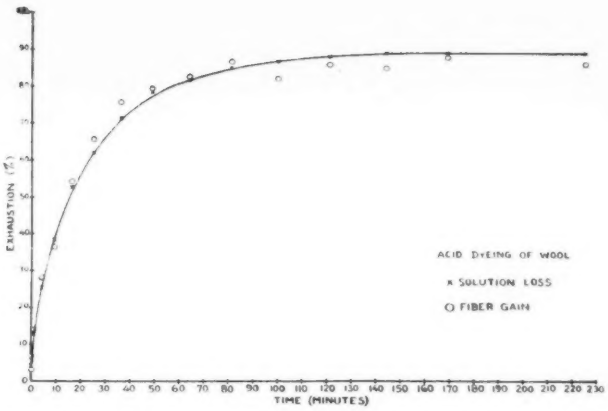

Figure 7
Exhaustion vs time

that had left the dyebath were calculated and expressed as percentages of the total dye in the system. A sample of the dyed fiber was analyzed, and the amount of dye in the fiber was expressed in the same way. In Table I the results are compared with those from the original, 324-minute dyeing, which was stopped in the usual way—by pouring the contents of the dye beaker into ice water. Table I shows the amount of dye lost from solution, the amount of dye found to be in or on the fiber sample, and the difference between the two values or the amount of dye that apparently was missing.

By examination of the results, it can be seen that the amounts of dye lost from solution in the two dyeings are not significantly different. However, the amount of dye found in the fiber sample was found to be much greater for the sample that was not rinsed; and, consequently, the amount of dye missing is only 11%, as compared with 29% that was missing in the case of the sample that was rinsed in ice water. For the sample that was not rinsed, some of the dye found in the fiber could have come from solution that could not be removed by squeezing out the sample. Assuming the sample to retain its own weight of dyeliquor, the amount of dye furnished would be only 0.088%, which is seen to be negligible. The data show that at least 18% of the dye in the system, or about two-thirds of the 29% that was missing in the first dyeing, was present in a surface film, which was removed by rinsing. The fact that the dye in solution (8%), the dye in the fiber (63%), and the dye in the interface (18%) then totals up only to 89%, leaving 11% of the dye unaccounted for, is not too surprising when the possible error associated with the measurements is considered. Since the amount of dye missing was calculated by subtraction of two measured values, each of which could be in error by as much as 2%, the difference could be in error by 4%. Similarly, subtracting the two differences increased the possible error to 8%.

TABLE I
Dye balance at 324 minutes

	Percent of Total Dye in System		
	Lost from Solution	*Found in Fiber*	*Missing*
Rinsed	92 ± 2%	63 ± 2%	29 ± 4%
Not rinsed	91 ± 2%	80 ± 2%	11 ± 4%
Dye in surface film (minimum)			18 ± 8%

The fact that this relatively rough experiment had definitely accounted for two-thirds of the missing dye and could easily account for more in view of the inaccuracies involved, and the absence of any other reasonable explanation led to the conclusion that all of the missing dye must be located in a liquid, interfacial film.

The percentage of dye in the surface film was calculated, for each dyeing time, by subtracting the percentage of dye found in the fiber from the percentage of dye lost by the solution. In Figure 6, the percentage of dye in the solution, the percentage of dye in the fiber, and the percentage of dye in the interfacial film are plotted against the time in minutes. At the start of the dyeing process, dye was removed rapidly from the solution and transferred partly to the fiber and partly to the interface. After two or three hours, the dye in the surface film reached a limit at about 29%. In the meantime, the fiber continued to take up dye more slowly, and appeared to be reaching an equilibrium of about 63% at four hours. There also was some indication that the dye removed from solution was tending toward an equilibrium at this time. After 350 minutes, adsorption in the fiber took place at an increased rate, leading to a true equilibrium about 20% higher. It is interesting to note that since very little dye left the solution at this time, the dye taken up by the fiber was supplied from the interface.

In order to determine whether this surface behavior is limited to dyeing with acetate dyes or is a general effect which is present in all types of dyeing, similar experiments were carried out using an acid dye on wool and a direct cotton dye on viscose rayon.

Original data for the dyeing of wool with Anthraquinone Blue B are shown in Figure 7. A curve was drawn as nearly as possible through the points representing the dye lost from solution. The points (circled) representing dye taken up by the fiber were plotted; and, in general, they were found to fall very close to the curve with a distribution on both sides of the curve. Therefore, it was decided that no surface film exists in the dyeing of wool with acid dyes.

Original data obtained from the dyeing of viscose rayon with Pontamine Sky Blue 6BX are shown in Figure 8; a smooth curve was drawn through the points obtained by measuring loss of dye from the bath. It can be seen that the circled points, representing the dye taken up by the fiber, fall quite close to the curve. Although more points lie below the curve, the difference is probably within experimental error and certainly is too small to prove the existence of a film similar to the one which was found to be present in the

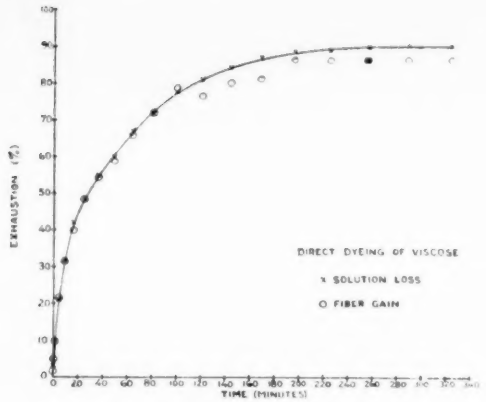

Figure 8
Exhaustion vs time

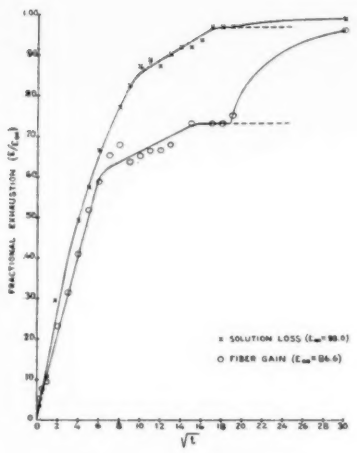

Figure 10
Fractional exhaustion vs square root of time

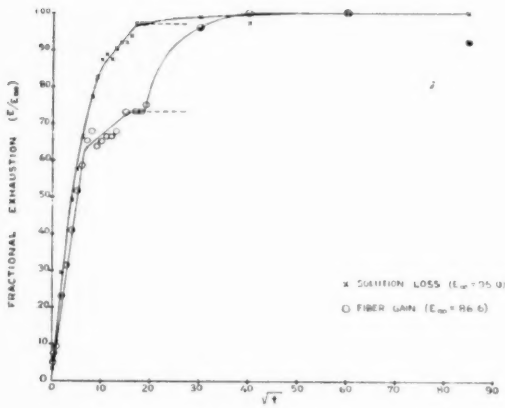

Figure 9
Fractional exhaustion vs square root of time

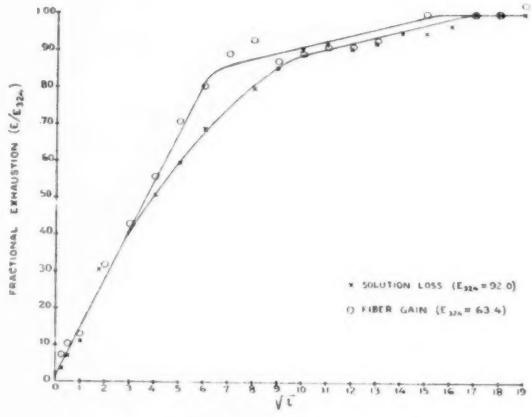

Figure 11
Fractional exhaustion vs square root of time

dyeing of cellulose acetate.

Since, in the dyeing of wool and viscose rayon, no appreciable difference in the exhaustion values was observed, whether determined by loss from solution or by fiber gain, it was decided that the presence of a highly concentrated surface film does not apply to all types of dyeing, but is peculiar only to disperse dyes.

An attempt was made to fit the data for the acetate dyeings to the following approximation to Fick's equation for diffusion in the steady state:

$$\frac{E}{E_\infty} = 2\sqrt{\frac{D.t}{\pi}}$$

where:

t is the time
E is the exhaustion at any time "t"
E_∞ is the equilibrium exhaustion
D is the apparent diffusion coefficient.

The equation assumes a constant concentration gradient, and a constant concentration of dye in solution at the surface of the fiber. Until dye reaches the center of the fiber, dyeing will approximate diffusion into a plane slab of material of infinite thickness. Although a constant concentration gradient has not been shown to exist in the dyeing of textile fibers, this equation has been found by Speakman and Smith (9) to apply quite well in the dyeing of mohair with Acid Orange 2G. They concluded that a layer of constant concentration must exist at the surface of the fiber. If this approximation does apply, the initial portion of a plot of the fractional exhaustion ($E/E\infty$) against the square root of time should form a straight line passing through the origin. Such a plot for the dyeing of cellulose acetate with Eastone Blue BB is shown in Figure 9. The fractional exhaustions were plotted for both solution loss and fiber gain, using their respective equilibrium values so that both curves would reach a final fractional exhaustion equal to 1.00. Figure 10 shows the initial portion of the same plot. Fairly good straight lines could be drawn for both sets of data for the initial part of the dyeing, which seems to indicate that loss of dye from solution and adsorption of dye by the fiber are both diffusion processes. The fact that the dye lost from solution is greater than the dye taken up by the fiber might indicate that the removal of dye from the bath occurs by diffusion into the film superimposed on the diffusion into the fiber.

If the increase in adsorption of dye following the first apparent equilibrium (at 324 minutes) is the result of a basic change in the system, it would probably be more correct to use these first equilibrium values in the calculation of fractional exhaustions. The fractional exhaustions E/E_{324} were plotted against the square root of time, as shown in Figure 11. It may be seen that the initial, straight-line portions of the curves are apparently the same line. In this case, the rate of transfer of dye to the surface film would be equal to or greater than the rate of

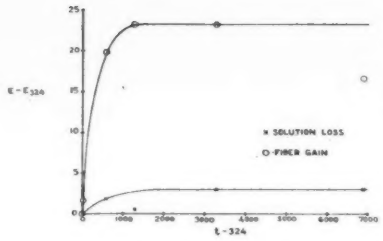

Figure 12
[E-E324] vs [t-324] for second dyeing period

diffusion in the fiber, since the rate measured is necessarily the slowest in the series of transfer mechanisms. The straight-line relationship holds longer for the Fiber-Gain curve than for the Solution-Loss curve, which might be expected since the loss of dye from solution is modified by the presence of an interfacial film between the solution and the fiber. Although these observations are not conclusive evidence that a fundamental change in the dyeing system occurs at about 324 minutes, they seem to lend support to the idea that such a change may occur. In order to investigate further, the dyeing after 324 minutes was considered as a separate process.

In Figure 12, the exhaustion minus the exhaustion at 324 minutes (E—E_{324}) was plotted against the time minus 324 minutes (t—324). The two curves obtained have a general shape which could indicate a second dye adsorption process beginning after the false equilibrium at 324 minutes. Calculated fractional exhaustion values $(E—E_{324})/(E\infty—E_{324})$, were plotted against the square root of (t—324), as shown in Figure 13. For both the Solution-Loss curve and the Fiber-Gain curve, it was possible to draw straight lines through the plotted points for the beginning of the second dyeing period, which was assumed to start at or near 324 minutes. Four points on each curve seemed to be sufficient justification for drawing the curves the way they are shown in Figure 12, although it was necessary to assume that one point on each curve was in error.

Figures 12 and 13 seem to furnish additional support to the theory that a change in the dyeing system occurs at about 324 minutes, which initiates a second dye-adsorption process. As shown by the plots of fractional exhaustion against the square root of time, the second dyeing process apparently took place by the same mechanism as the first, which was believed to be governed by diffusion.

Although, in Figure 11, it was shown that a plot of the fractional exhaustions (E/E_{324}) against the square root of the time (t) reduced the first parts of the Solution-Loss and Fiber-Gain curves to the same straight line and brought them together at the first equilibrium, differences in the central portions of the curves still existed. It was later found that, by plotting the same fractional exhaustion values against ratios of the time (t) to the time of half-dyeing ($t_{1/2}$), the curves could be brought more closely together. The time of half-dyeing is the time required for the fiber to take up half as much dye as it would adsorb at equilibrium. Since the amount of dye lost from solution was different from the amount of dye taken up by the fiber, this definition strictly should not apply to the solution measurements. However, the time of half-dyeing for the solution-loss data was taken as the time required for the dyebath to lose half as much dye as it would lose at equilibrium, in order that a similar parameter for solution measurements could be obtained. The plot is shown in Figure 14, where a single, smooth curve was drawn as nearly as possible through all the plotted points. Except for one region where four consecutive Fiber-Gain points lie above the curve and four Solution-Loss points fall below the curve, practically the same curve could be drawn for either set of data.

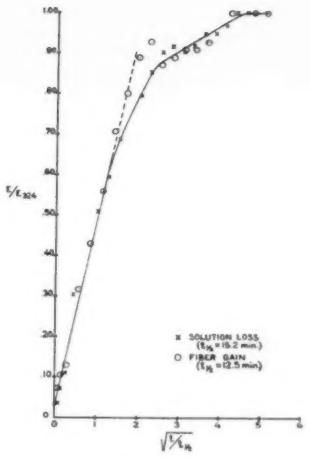

Figure 15
E/E_{324} vs $\sqrt{t/t_{1/2}}$

Even closer agreement between the curves was obtained when the fractional exhaustions were plotted against the square roots of values of $t/t_{1/2}$. As shown in Figure 15, the two sets of data agree very closely, again with the exception of four points. A solid line was drawn for all points, but in the region where the deviations occur the solid curve was made to follow the Solution-Loss data in order to obtain the best smooth curve. The broken line shows the trend of the Fiber-Gain points

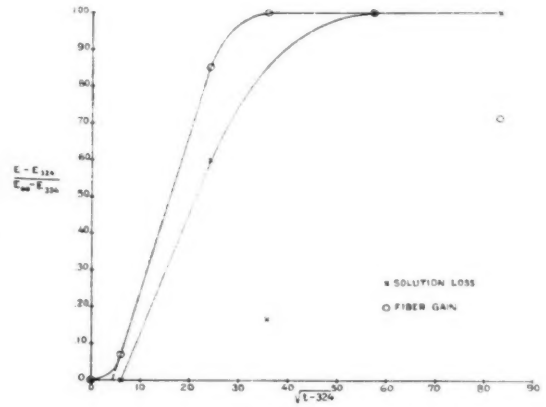

Figure 13

$\left[\frac{E-E_{324}}{E\infty-E_{324}}\right]$ **vs** $\sqrt{t-324}$ **for second dyeing period**

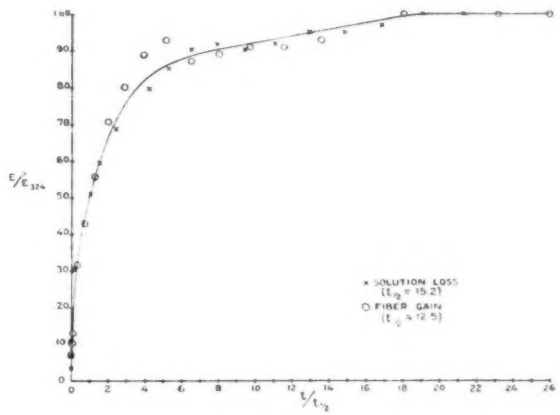

Figure 14
E/E_{324} vs $t/t_{1/2}$

to continue the initial, straight-line relationship.

There is no theoretical basis for the plots shown in Figures 14 and 15. However, the fact that the Solution-Loss curve and the Fiber-Gain curve can be made to coincide so well when each set of data is referred to its own parameters is a definite indication that adsorption of dye by the fiber and loss of dye from solution occur by the same basic process regardless of the presence of a surface film which causes quantitative differences.

The increased adsorption of dye following the false equilibrium at 324 minutes might be the result of a change, either in the dye or the fiber. An increase in the affinity of the dye could account for the sudden increase in dyeing rate, but a change in the dye affinity seems highly improbable and would be difficult to explain. If a change in the fiber is considered, the dyeing behavior could be attributed to an occurrence similar to the one observed by Marsden and Urquhart (*4*) in a study of the adsorption of phenol, from aqueous solution, by cellulose acetate sheet material. A plot of the amount of phenol taken up by the cellulose acetate against the concentration of phenol in solution showed an abrupt break when the concentration reached a critical value, which caused the acetate to swell and become opaque. They concluded that the swelling, which caused greatly increased water absorption, disrupted the internal structure of the acetate film, making available many more sites upon which the phenol could be held, and initiating a second Langmuir adsorption isotherm based on a larger number of sites.

It was believed possible that the acetate dye itself might be capable of exerting a similar swelling action on cellulose acetate, in which case the increased adsorption of dye following the first equilibrium does not seem unreasonable.

In an attempt to explain the observed acetate dyeing behavior, several possibilities were considered.

The possibility that the dye is largely surface active could account for the formation of an interfacial film having a higher concentration than the dyebath. In general, a surface-active agent is characterized by a linear, hydrophobic, molecular structure having a highly polar, or solubilizing, group at one end. Disperse dyes, however, do not have this type of structure; and therefore, it seemed very unlikely that surface activity of the dye could be responsible in this case.

Another possibility considered is that of the preferential wetting of a finely divided solid material by two immiscible liquids, which would be the water and the cellulose acetate in the acetate dyeing system. Provided that the contact angles between the solid and both liquids are finite, there would be a tendency for the solid dye particles to collect in a third-phase interface.

A third possible explanation for the interfacial film seemed more reasonable, in view of the fact that acetate dye particles in the dyebath are known to exist in a wider range of sizes than those of other types of dyes—even those which form colloidal solutions. Assuming that acetate dyeing takes place by diffusion of the dye through intermicellar canals in the fiber, as seemed to be indicated by the manner in which the data was found to fit the diffusion equation, it would be quite certain that only a fraction of the dye particles would be small enough to penetrate into these canals. Assuming a high affinity between the dye and the fiber, those particles which were too large to penetrate would probably be retained in a film between the fiber and the solution. Since, in this case, the interface would be confined to the external surface area of the fiber, which would probably be inadequate to accommodate so much dye in a single layer, it would be necessary to assume that the dye is deposited in several layers.

If the dye produced a swelling of the fiber, an increase in the size of the intermicellar canals would result. This would permit larger dye particles, which had previously been confined to the surface film, to enter; and, consequently, there would be an increase in the rate of dyeing.

Regardless of the mechanism of the dyeing or the cause of the film formation, it is doubtful if the entire volume of the substratum is available to the dye. The examination of textile fibers by X-ray methods has shown the existence of "crystallites," or areas where the molecules are regularly arranged in an orderly manner. These crystallites do not make up the whole of the fiber substance, but are interspersed throughout amorphous regions where the fiber molecules are loosely packed in a random manner. It is generally believed that even individual dye molecules are too large to be able to penetrate the crystallites, and that dyeing is possible only in the amorphous regions of the fiber. Since a single molecule may pass through both amorphous and crystalline regions, swelling would tend to make the fiber more amorphous and enlarge the volume available for penetration by the dye. With more volume available, more dye could be taken up by the swollen fiber and a higher equilibrium exhaustion would be attained.

Assuming that the dye actually did produce a swelling of the fiber at approximately 324 minutes in the cellulose acetate dyeing, it was believed possible to obtain a rough measure of the extent of the swelling by making use of an equation derived by Vickerstaff (*11*) for the calculation of dye affinities:

$$-\Delta\mu^\circ = RT \ln \frac{[D]_f}{[D]_s} \cdot \frac{1}{V}$$

where:

$-\Delta\mu^\circ$	is the difference in "standard chemical potential"
$[D]_s$	is the concentration of dye in solution (moles per liter)
$[D]_f$	is the concentration of dye in the fiber (moles per kilogram of dry fiber)
V	is the volume of fiber available to the dye (liters per kilogram of dry fiber)
T	is the absolute temperature (degrees Kelvin)
R	is the gas constant (calories per degree Centigrade per mole).

Hence:

$\frac{[D]_f}{V}$	is the true concentration of dye in the amorphous portion of the fiber.

The difference in standard chemical potential, $-\Delta\mu^\circ$, as defined by Vickerstaff (*12*), "is a measure of the tendency of a dye to move from its standard state in solution to its standard state on the fiber and is a quantitative measure of the affinity of the dye for the fiber". This equation is based on the assumption that the dye in the fiber is in solid solution or is diffusely adsorbed, and that the dye is unionized in both the dyebath and the fiber. Concentrations of dye in the solution and the fiber have been substituted for the respective activities. Such a substitution may be justified only when dealing with unionized substances in very dilute, true solutions. Since it is extremely doubtful if these conditions all exist in acetate dyeing, particularly in the fiber phase, the equation is at best only a rough approximation.

Using the subscripts 1 and 2 to designate conditions before and after swelling, respectively, the following expressions may be written:

Before Swelling:

$$-\Delta\mu^\circ_1 = RT \ln \frac{[D]_{f1}}{[D]_{s1}} \cdot \frac{1}{V_1}$$

After Swelling:

$$-\Delta\mu^\circ_2 = RT \ln \frac{[D]_{f2}}{[D]_{s2}} \cdot \frac{1}{V_2}$$

Since the affinity of the dye for the

fiber would not be expected to change.

$$-\Delta\mu^{\circ}_1 = -\Delta\mu^{\circ}_2$$

and:

$$RT \ln \frac{[D]_{f1}}{[D]_{s1}} \cdot \frac{1}{V_1} = RT \ln \frac{[D]_{f2}}{[D]_{s2}} \cdot \frac{1}{V_2}$$

Therefore:

$$\frac{[D]_{f1}}{[D]_{s1}} \cdot \frac{1}{V_1} = \frac{[D]_{f2}}{[D]_{s2}} \cdot \frac{1}{V_2}$$

and the ratio of the swollen volume (V_2) to unswollen volume (V_1) is given by:

$$\frac{V_2}{V_1} = \frac{[D]_{s1}\,[D]_{f2}}{[D]_{s2}\,[D]_{f1}} \cdot$$

Concentrations of dye in the solution and the fiber for the first and final equilibria in the acetate dyeing were substituted in the equation, and the ratio V_2/V_1 was calculated. (It was not necessary to convert the measured concentrations to moles per liter and moles per kilogram, since the concentrations need only be in the same units.)

$$\frac{V_2}{V_1} = \frac{(8.0)(86.6)}{(5.0)(63.4)} = 2.19$$

A corresponding value was calculated using the amounts of dye in the interfacial film rather than the concentrations of dye in solution:

$$\frac{V_2}{V_1} = \frac{(28.6)(86.6)}{(9.8)(63.4)} = 3.99$$

(The amount of dye in the film at the final equilibrium was assumed to be the average of the last three points.)

The calculated figures would seem to indicate that the volume of fiber available for dyeing after swelling was either double or four times that available in the unswollen fiber. In order for a fourfold increase in available volume to be possible, it would be necessary for the fiber to have a minimum of 75% crystallinity before swelling. Even if the available volume were only doubled by swelling, it would mean that the unswollen fiber must be at least 50% crystalline. This seems hardly credible, since cellulose acetate is generally believed to have a low degree of crystallinity.

However, if dyeing occurs from a very dilute, true solution which is maintained at saturation by the presence of the solid, dispersed, dye particles, it would be incorrect to use the measured concentrations of dye in the bath at the first equilibrium and the final equilibrium. Although the concentration of a saturated solution of the dye is not known, it would be true that $[D]_{s1} = [D]_{s2}$ and the volume-ratio equation would reduce to the following expression:

$$\frac{V_2}{V_1} = \frac{[D]_{f2}}{[D]_{f1}} = \frac{86.6}{63.4} = 1.37$$

In this case an original crystallinity of 27% would be sufficient for V_2 to be 1.37 times greater than V_1, and it at least seems possible that such a degree of swelling could take place.

It is quite possible that acetate dyeing takes place by a mechanism of adsorption upon sites in the fiber; for example, by hydrogen bonding with the acetyl groups of the cellulose acetate. Such a mechanism was suggested by Marsden and Urquhart (*4*) for the adsorption of phenol. Commercial cellulose acetate, however, is not completely acetylated. Therefore, there is still a certain number of hydroxyl groups remaining which should also be capable of forming hydrogen bonds with the dye. According to Vickerstaff (*13*), commercial cellulose acetate corresponds roughly to a diacetate, but "*Matthews' Textile Fibers*" (*5*) states that the acetyl content is about halfway between that of the triacetate and the diacetate. It may not be too much in error, then, to assume that the cellulose acetate contains 2.25 ester groups and 0.75 hydroxyl groups per glucose unit, which would make a total of 3.00 hydrogen bonding groups. If the dye is adsorbed preferentially on the acetyl groups followed by a secondary absorption on the hydroxyl groups, the ratio of the total available groups to the acetyl groups is given by:

$$\frac{3.00}{2.25} = 1.33 \cdot$$

It is interesting to note that this figure compares quite closely with the calculated value of 1.37, the ratio of the volume of fiber available to the dye after an assumed swelling to that available before swelling; or, equally, the ratio of the number of sites available after swelling to the number of sites available before swelling.

From the plots of fractional exhaustion against the square root of time, both before and after 324 minutes, which are shown in Figures 11 and 13, the apparent diffusion coefficients were calculated. The slopes of the best, initial straight lines (obtained by the method of averages) were calculated and substituted in the diffusion equation, which was then solved for the apparent diffusion coefficient (D):

$$\frac{E}{E_\infty} = 2\sqrt{\frac{D.t}{\pi}} = 2\sqrt{\frac{D}{\pi}} \cdot \sqrt{t}$$

$$\text{Slope} = S = 2\sqrt{\frac{D}{\pi}}$$

$$S^2 = 4 \cdot \frac{D}{\pi}$$

$$D = \frac{\pi}{4} S^2$$

The calculated values of the diffusion coefficient are shown in Table II where the subscripts 1 and 2 denote the first dyeing period (before 324 minutes) and the second dyeing period (after 324 minutes), respectively. As would be expected, the values of D_1 are much greater than the values of D_2. For the first dyeing period, the coefficients determined for Solution Loss and Fiber Gain appear to be the same. The corresponding values of D_2 may also be the same since the absolute difference between them is small, although one is 1.67 times greater than the other.

TABLE II

Comparison of apparent diffusion coefficients

	D_1	D_2
Fiber Gain	0.0137	0.0015
Solution Loss	0.0170	0.0009

D_1 (before 324 minutes)
D_2 (after 324 minutes)

An attempt was made to find a mathematical expression relating the amount of dye in the interfacial film to the dyeing time. The amount of dye in the film, as shown by the plot of the experimental data in Figure 6, increases quite rapidly to a maximum, and then decreases much more slowly. Although the last two points seem to show a tendency for the amount of dye in the film to increase at very long dyeing times, such an increase would be very unlikely since the amount of dye taken up by the fiber and the amount of dye lost from solution appear to be at equilibrium. Consequently, it was assumed that the curve levels out at about 9%. Since the amount of dye in the film was determined by subtracting the amount of dye in the fiber from the amount of dye which had left the solution at a given time, it seemed reasonable that the proper equation for the data should also contain a difference of two quantities. It was believed that the following form of equation might fit the data, provided that the correct constants could be found:

$$[D]_i = k\,(e^{-at} - e^{-bt})$$

where:

$[D]_i$ is the amount of dye in the interfacial film expressed as a percentage of the total dye in the system;

t is the time in minutes;

a, b, and k are constants, and "b" is greater than "a".

The two apparent diffusion coefficients, D_1 and D_2, which were obtained from Fiber-Gain curves before and after 324 minutes, were substituted for "b" and "a", respectively; and after evaluating the constant "k", the following equation was obtained:

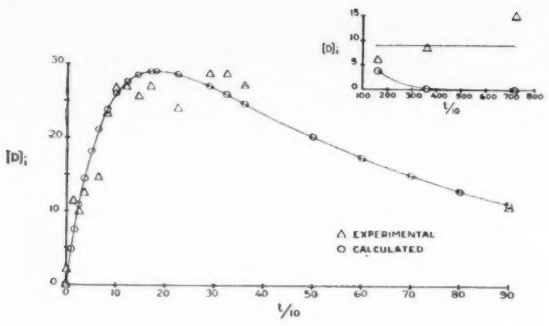

Figure 16
$[D]_i$ vs t/10

$$[D]_i = 42.7\ (e^{-D_2 t} - e^{-D_1 t})$$
$$D_1 = 0.0137$$
$$D_2 = 0.0015$$

The experimental values and the calculated values were plotted against t/10 (for convenience); and, as shown in Figure 16, the curve drawn through the calculated points agrees very closely with the experimental data up to 900 minutes. There is reasonably good agreement even up to 1600 minutes. As the dyeing time becomes greater, the curve for the equation approaches the line: $[D]_i = 0$ as an asymptote; but the experimental points were taken to indicate a leveling-out of the curve at approximately 9%. Therefore, when the dyeing time becomes very great the calculated values no longer agree with the experimental data. However, the equation does offer theoretical possibilities, since it contains the apparent diffusion coefficients, to which the amount of dye in the surface film might well be related.

CONCLUSIONS

1) It has been established that an interfacial, liquid film exists in the dyeing of cellulose acetate with disperse dyes, and that it contains an appreciable amount of dye.

2) The interfacial film persists over the entire time of dyeing———even up to 7200 minutes, which is equivalent to five days; but it varies in the amount of its dye content during the dyeing operation.

3) For the first several hours of the dyeing process, the amount of dye in the surface film is increasing. It finally becomes constant, for a period of approximately three hours, during which time an equilibrium between solution and dyed fiber seems to be in the process of being established. At the end of the three-hour period, the apparent equilibrium is disturbed in some manner, leading to the adsorption of considerably more dye by the fiber.

4) In this second period of dyeing, the dye comes principally from the interfacial film as shown by a large decrease in the amount of dye in the film.

5) There is some indication that the increased dye adsorption following the first equilibrium may be due to a swelling of the cellulose acetate by the dye.

6) There is also some indication that the acetate dyeing process is governed by diffusion, since a plot of the fractional exhaustion against the square root of the dyeing time yields a straight line during the initial period of dyeing.

7) The formation of an interfacial film is a phenomenon peculiar to dyeing with acetate dyes and does not occur in the dyeing of viscose rayon with direct cotton dyes or in the dyeing of wool with acid dyes.

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Abstracts

Finishing Blends of Dacron and Cotton

Hunter, R L, *Textile Bull* **83**, 83-8, July, 1957

Blends of Dacron and cotton have grown within the last four years into a whole series of fabrics ranging from lingerie to work clothing.

The author describes some of the problems peculiar to Dacron, and suggests ways for overcoming them. First, there is pilling. Here, experience has shown that the two best control processes are heat-setting, at 385-430°F, and singeing. However, these high temperatures create dyeability problems, since heat-setting (prior to dyeing) at 275-390°F reduces the dyeability of Dacron, while above 390°, it is sharply increased. To avoid shading, a uniform temperature is necessary. Also, in heat-setting after dyeing, dye sublimation may occur above 350°F.

Regarding dimensional stability, shrinking problems in laundering or pressing of garments can be avoided by adequate heat-setting in finishing. The fabrics should be completely relaxed throughout the finishing operations.

Since Dacron is more sensitive to alkalis than cotton, kier-boiling with strong caustic should be avoided. Mercerization, however, is beneficial to these blends because it improves the absorbency and hand of the fabric.

Standard peroxide bleaching is recommended for the cotton fibers, but peroxide does not bleach the Dacron to any extent.

Two dyeing methods are proposed. The Dacron component can be dyed with disperse dyes plus carriers, or by the Thermosol method in which the fabric is padded with the disperse dye and then heat-treated. In either case the cotton is dyed later. Pastel shades can be vat-dyed.

Finishes such as cationic softeners can be applied during frame finishing, which is followed by compressive shrinking.

Resin treatments of Dacron/cotton

(concluded on page 776)

WITH GLYCERINE FROM FIBER TO FABRIC
PART I

EVA A PAROLLA and CARL Z DRAVES

INTRODUCTION

IN THE words of E Scott Pattison, "Glycerine is a modern miracle polyol, not just a historical curiosity" (*1*). Its important place in today's textile industry effectively illustrates this point.

Discovered by Scheele in 1779, glycerine found its first application in textile processing about 95 years ago, in France, when it was used to reduce thread breaking in the manufacture of fine muslins. The moisture-absorbing and -retaining properties of glycerine made it possible to process these extremely delicate thin fabrics without maintaining an excessively humid atmosphere in the mills (*2*). From this initial use in France, the employment of glycerine has spread into a multiplicity of textile operations throughout the world.

Thus, in addition to its earlier use as a humectant and spinning lubricant, glycerine soon gained wide acceptance as a dyeing and printing assistant, as a softener, sizing aid, and plasticizer, until today it has come to serve a wide variety of purposes in textile finishing. For example, antistatic preparations, waterproofing or flameproofing compositions, wrinkle-resistant and gasproof finishes frequently contain glycerine. Most of these special-finish formulations are based on alkyd resins, many of which, in turn, are esters of glycerine and phthalic anhydride.

The sum of these applications in textiles constitutes but a small part, perhaps less than 2%, of the total consumption of glycerine in this country. The knowledge that the uses of glycerine in numerous other fields are keeping pace with modern industrial developments may therefore assure the textile technologist of a continued and steady supply.

SUPPLY AND DEMAND

A brief side glance at production figures shows that the domestic output of refined glycerine rose from 126.5 million lb in 1936 to 148.6 million lb in 1946, representing an increase of 17.5%, whereas the 1956 output rose to approximately 250 million lb, an increase of 97.6% over 1936 (*3*). Synthetic glycerine has been partly responsible for this rapid rate of growth.

Less than ten years ago commercial glycerine was only a byproduct, the bulk of it having been obtained from soap manufacture, and the remaining volume from fat splitting and the production of fatty alcohols (*4*). Although synthetic glycerine production did not begin until 1948 (*4*), a synthetic output approximating 30% of the total production was achieved by 1955 (*5*). New facilities for manufacturing synthetic glycerine tend to encourage hopes for an even greater output in the future, and for gearing glycerine production more closely to demand than has sometimes been possible in the past (*5, 6*). A 1956 forecast estimates synthetic capacity alone at 110 million lb per year (*1*).

Furthermore, this accelerated growth in production reflects—and may well foreshadow—an increasing use of glycerine in many applications. Total domestic consumption in 1955 reached a "near-record" 235 million lb (*1*). A peak had occurred in 1950, at 240 million lb, of which 4 million lb, or 1.66%, went into textiles (*7*). This figure was quoted again in 1955 by M A Lesser as the approximate quantity of glycerine "consumed annually by the textile industry" (*8*).

Only slightly more than 2.2 million lb had been used for this purpose in 1943. Allowance should be made for the fact that glycerine was an allocated material during most of World War II, and that the textile industry was forced to use substitutes, which, incidentally, did not always prove satisfactory (*9, 10*). In view of wartime restrictions, the 2.2-million-lb figure compared favorably with the prewar figure of 2.3 million lb for 1940. When glycerine was released for unlimited civilian use in 1944, the textile-consumption estimate for that year was 2.5 million lb (*9*). The 4 million lb consumed in 1950 exceeds this amount by 60%.

MAN-MADE FIBERS——The increase in the domestic production of man-made fibers within the last 16 years may be taken as a good indication of the growing potential of the textile industry and, by inference, of a continuing need for more glycerine. The total output of man-made fibers, which has more than tripled in these years, includes both the older category of rayon and acetate, and the newer series of noncellulosic and glass fibers. A breakdown of production figures for key years is shown in Table I, which represents a partial reproduction of data published by the Textile Economics Bureau, Inc, N Y 16, N Y (*11*).

TABLE I
U S Production of Man-made Fibers
(million lb)

	Textile Glass	Noncellulosic	Total	Rayon & Acetate	Grand Total
1940	1.4	3.2	4.6	471.2	475.8
1950	23.5	122.4	145.9	1,259.4	1,405.3
1954	59.2	284.6	343.8	1,085.7	1,429.5
1955	75.8	379.3	455.1	1,260.7	1,715.8
1956	96.9	399.9	496.8	1,147.9	1,644.7

Synthetic Fibers. Obviously, the so-called "synthetic fibers" share significantly in this rosy production picture. During the time in which the output of rayon and acetate slightly more than doubled, the total for textile glass and noncellulosic fibers increased exactly 108-fold, and the output of noncellulosic synthetic fibers alone, almost 125-fold. This phenomenal growth is definitely of interest as a potential source of demand for glycerine, since many well-established uses of the product have already been adapted to the processing of such fibers.

ALKYD RESINS——The largest single use of glycerine lies in the manufacture of alkyd resins (*12*). The 72 to 80 million lb of glycerine used annually for this purpose accounts for 18 to 20% of the total U S production of alkyds (*1*). Although glyceryl phthalate ester resins as well as other alkyds are mainly used in paints, varnishes, enamels, and lacquers, they are also valued as versatile textile finishing agents and have even been proposed as intermediates for making fabrics (*2, 13*).

PROPERTIES

What are some of the properties which make glycerine so eminently suitable for its varied textile uses? It is a clear free-flowing viscous liquid, completely miscible with water and the lower alcohols or glycols, as well as phenols. To a lesser extent it is miscible with aniline or organic solvents, such as ether and acetone, yet it will dissolve many organic and inorganic compounds. Glycerine is insoluble in fats, oils, and other hydrocarbons, including chlorinated hydrocarbons (*14*). The more nearly pure grades of glycerine are white to pale yellow in color and possess at most a faint, characteristic odor; their taste is distinctly sweet and warm.

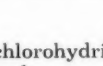
PHYSICAL PROPERTIES——Apart from solubility and useful solvent characteristics, its physical properties most significant in textile applications are heavy viscosity, low vapor pressure, and outstanding hygroscopicity. These are responsible for the lubricating, softening, and plasticizing action of glycerine, for its bodying and humectant qualities, and for its ability to absorb considerably more than its weight in water (*15*). The affinity of glycerine for textile fibers (*10*) and its nonfoaming characteristics are other points of importance.

Glycerine* has a molecular weight of 92.09. It possesses a high boiling point, 290°C (554°F) at 760 mm, and a low melting point, 18.0°C (64.4°F)—actually, it tends to supercool and is hard to crystallize (*4, 14*). These properties make it valuable in many applications in which other solvents fail. The specific gravity of glycerine at 20/20°C (68/68°F) is 1.26362; viscosity at 20°C, 1410 cps, as compared with 1.005 for water. Glycerine has a surface tension lower than that of water but higher than that of most organic solvents. Its unusually low compressibility is about one-half that of water. Its high flash point, 177°C (350.6°F), and fire point, 204°C (399.2°F), are significant safety factors (*14, 15*). For detailed data, including tables, the authors recommend two brochures available from the Glycerine Producers' Association (*4, 15*).

CHEMICAL PROPERTIES——Glycerine (sometimes spelled *glycerin*) is a saturated trihydric alcohol, $CH_2OH.CHOH.CH_2OH$. Chemically, it is more often referred to as glycerol, or *1,2,3-propanetriol*. Its two terminal hydroxyl groups function as primary alcohols and, as such, are more reactive than its secondary-alcohol center group.

Reactions. Glycerol can take part in any of the reactions common to alcohols, such as replacement of one, two, or all three hydroxyls by halogens or amine groups, ether formation, and esterification. Conditions may be varied to control the number of hydroxyls participating in a reaction, or to obtain mixed derivatives (*4, 14*).

Derivatives. Among the numerous derivatives of glycerol useful in textile processing are dichlorohydrins, applicable to the etherification of certain cellulosic textile materials (*9*);



epichlorohydrin, $CH_2\text{-}CH.CH_2Cl$, employed as an intermediate for organic dyes with a high degree of water solubility (*16*); "monoglycerides," effective as emulsion stabilizers. Although their name would seem to identify these products as esters of one mole of fatty acid and glycerol, commercial "monoglycerides" are actually mixed esters containing, in addition, appreciable quantities of the di- and triester (*15*).

Of all derivatives, however, alkyd resins are unquestionably the most important textile-finishing aids. Most alkyds are esters of glycerol and phthalic acid; special effects are obtainable by the use of other polybasic acids, such as maleic, sebacic, or succinic (*14, 17*). Glycerol-rosin esters, called "ester gums," are sometimes used to modify alkyd-resin finishes (*14, 18*).

Stability. Under normal use conditions, glycerine possesses a high degree of chemical stability. This property is essential to its successful utilization in textiles, which depends primarily, except for alkyd-resin use, on the physical properties of glycerine.

The presence of iron or copper in containers holding glycerine or its solutions should be avoided, if possible, or offset by the addition of inhibitors. Otherwise, the salts of these metals act as catalysts causing glycerine to be oxidized on prolonged storage or heating (*4, 14*).

PHYSIOLOGICAL PROPERTIES——Glycerine is nontoxic and readily digestible in reasonable quantities. It forms in the body as a result of the digestion of fats and is used as a sweetener in foods and pharmaceuticals. The nonirritating qualities of glycerine are attested to by its exceedingly common use as an emollient in cosmetics.

*Data in this paragraph refer to 100% pure glycerine.

APPLICATIONS

A. Preparation of Textiles

Glycerine is a textile-conditioning agent used widely in the lubrication, sizing, and softening of yarn or fabric. Its effectiveness in these and similar applications is due mainly to viscosity and hygroscopicity, both properties contributing to the plasticizing action. Hygroscopic, or humectant, qualities also account for the utilization of glycerine in special treatments, such as processes to increase the wearability of fabrics or to prevent static charges on fibers. Because of impermeability to poison gas, particularly "mustard," glycerine finds application in gas-resistant finishes. Water solubility is an asset when glycerine serves as a lubricant. This obviates the need for strong scouring agents, which tend to injure the fabric but which must often be used to remove other lubricating oils.

Glycerine itself does not significantly affect fiber strength. In recent tests measuring the chemical resistance of eight textile fibers to each of 53 different chemicals, glycerine reduced only slightly the strength of acetate, rayon, cotton, silk, and wool; left nylon entirely unaffected; and actually produced a slight increase in the strength of both Dacron polyester and Orlon acrylic fiber. The test fibers were exposed to 100% glycerine at 210°F for ten hours (*19*).

As an additive to lubricating compositions, sizes, or various finishes, glycerine acts as a plasticizer, solvent, and penetrant. It prevents drying out and caking on the fiber, eliminates the dusting of sizes, and may aid in dispersing water-insoluble lubricating oils applied from a water bath (*20*).

LUBRICATION——Glycerine has been used successfully to lubricate all types of fibers in operations including spinning, twist setting, knitting, and weaving. Glycerine is oily and smooth enough for this purpose, without being sticky or tacky. Moisture retention is an important feature in that water itself has a softening and plasticizing effect on textile fibers. The value of glycerine as a sizing ingredient is based on the same principles.

Lubricant Preparations. A fairly recent patent describes, as follows, the composition of a water-soluble lubricant free from fatty and mineral oils (*21*):

1) A component to cause mutual adhesion of the fibers, such as a sugar or its ether or ester, a sulfite liquor, polypeptide, etc.
2) A viscous component that will lubricate the fibers without loosening them, eg, a polyglycol, a polyoxide wax or a similar

water-soluble compound, or a surfactant, eg, ammonium oleyl sulfate.

3) A component to increase moisture retention by the fibers, such as a polyhydric alcohol, viz, glycerol, a glycol, or its water-soluble ether.

A very different type of lubricant may be made by reacting glycerine with a mixture of ethylene oxide and propylene oxide. The trihydroxy polyoxyalkylene glyceryl ethers thus obtained are mixtures of complex compounds whose viscosity changes but slightly with temperature. Besides stability to air and noncorrosiveness to metals, this series of lubricants exhibits unusual miscibility with many organic compounds, as well as with water. These and other properties were developed for the express purpose of creating lubricants which would be of value in compounding hydraulic-brake fluids, but they are also useful in textile processing (*22*).

Action on Nylon. In searching for a liquid that would prevent friction by spreading and adsorbing on nylon, members of the Naval Research Laboratory in Washington, D C, evaluated glycerine as one of a group of lubricants. This study proved of special interest in that it gave evidence of hydrogen bonding between glycerine and the nylon amide groups located on the surface. None of the compounds did too well on a nylon-nylon combination; however, on a steel-nylon interface glycerine proved far more effective than did a less viscous substance, a diol. Because of the distances between the amine-group adsorption sites, lower-molecular weight compounds appeared to have difficulty adsorbing on nylon. Glycerine and other polyhydric alcohols, long-chain fatty acids, and higher amines possess polar groups, which can be adsorbed by steel or the amide groups in nylon (*23*; see also *23a*).

Plasticizing Action. In contrast to the above hints of very modern uses, the following two applications are reminiscent of glycerine's earliest role in textiles: One is the lubrication of delicate threads or fibers, where glycerine prevents breakage and subsequently eliminates the need for harsh scouring (*18*). The other is the addition of glycerine to a soaking bath for raw silk. The bath readies the silk for knitting or weaving by making it soft and pliable and by humidifying the natural gum, which acts as a sizing agent. Manufacture at uncomfortably high temperatures in an atmosphere overcharged with moisture thereby becomes unnecessary (*18*).

Wearability. Of a similar nature are various procedures invented for the purpose of increasing the wearing qualities of textiles. A treatment for brittle fabrics with low fat content, described by Hillbring in 1939, provides for a machine dispensing a flow of glycerine at a rate of ½ to 4½ lb per 221 lb fabric. The method yields textiles possessing a softer hand and improved wearability (*24, 25, 26*).

Three years later Sebrell obtained patents (US 2,295,429 and Can 406,-416) on a process for decreasing runs and thereby prolonging the life of knitwear, particularly stockings. It consists in coating the threads with a composition containing glycerine. The fibers are thus strengthened, and the loops of knitted goods are allowed to slide over one another with a minimum of friction. This helps protect hose against the strain exerted on it by the wearer (*26a*).

Action on Wool. An early British patent (Brit 333,949; 1928) mentions glycerine as a suitable sizing agent and lubricant for wool as well as other textiles (*27*). A later one (Brit 547,667; 1942) claims that wool and other textile fibers can be processed more easily on the addition of oils containing a mixed ester of glycerine and a long-chain fatty acid as a scouring agent; these oils are removable by washing (*28*). Greasy, incompletely scoured wool may be treated very successfully with 20 to 30% glycerine on weight of wool (*27*).

In 1940 a Russian journal published a method for lubricating French worsted fabrics with a water emulsion containing pure coriander oil, ammonia, and technical glycerine (*28*). Another attempt to employ glycerine in the oiling of wool resulted in superior cleanliness of the final product and eliminated the static electricity usually encountered in carding (*29*).

Spinning. Hirai of Japan conducted a series of experiments to determine the relationships that exist between various factors and the spinnability of lower-molecular weight liquid substances. In the course of studying the proper ratio between concentration and spinning velocity, he found that a system containing glycerine at a concentration exceeding 93% is spinnable at 59°F (*30*). He also discovered that primary-alcohol compositions may be spun at lower temperatures in the presence of glycerine (*31*).

According to a patent granted to British Celanese, Ltd (Brit 431,964), a glycerine-containing lubricant is added to cellulosic spinning solutions or to finished fabrics. Another British Celanese, Ltd, patent (Brit 450,420) recommends the use of compositions consisting of soap, oil, water, and glycerine to lubricate cellulose ester or ether fibers, as well as other types of material (*18*). An American patent (U S 2,198,000) indicates that compounds containing glyceryl esters may be used effectively to oil cellulose acetate or similar yarns during spinning, knitting, or weaving (*32*). Other glycerine derivatives applicable to these processes as lubricants and softeners for cellulose acetate yarns are butylideneglycerol and similar compounds (US 2,153,136) (*28*).

U S Patent 2,198,000 also claims, as does Brit Patent 452,227, that formulations containing glyceryl esters or glycerine are useful in lubricating rayon staple-fiber yarns in the process of manufacture (*18, 32*). Waldman and Chwala (Austrian 154,478) refer to glycerine plus acetone or benzaldehyde as valuable ingredients of lubricating compounds for rayon or other fibers (*33*).

In a patent assigned to American Viscose Corp, Moss shows how the extrusion of viscose into filaments or films can be improved by the use of an ethylene oxide-polyhydric alcohol condensate in the spinning solution. This condensate, which is composed of more than nine moles of ethylene oxide per mole of polyhydric alcohol, eg, glycerol, is employed in a concentration exceeding 0.001% of the spinning bath. More even sizing and reduced breakage of filaments are reported (*34*).

Similarly, Calton and O'Brien (U S 2,555,300) propose extruding a solution of wet-spun acrylonitrile polymer into a coagulating bath of hot glycerine; the yarn is then dipped in water and entered into a final glycerine bath. This method produces yarn of greater tenacity (*35*).

Bruson and Riener find that the viscosity of polymeric polyacrylonitrile spinning solutions can be reduced by the addition of small quantities of a water-soluble polyhydric alcohol, such as glycerine, to a hot (194-212°F) ethylene carbonate spinning solution of the polymer. As increasing amounts of polyhydric alcohol are added, the solution decreases in viscosity until gelation sets in (*36*).

Knitting and Weaving. Glycerine may be added to solutions used in the twist setting and conditioning of yarns prior to weaving. It has a weighting effect and may shorten the time of twist setting by stabilizing the regain of moisture and by serving itself as a substitute for the water that tends to evaporate before the twist is set (*37*).

Glycerine is generally used as a conditioning agent and lubricant in the weaving or spinning of wool, silk, cotton, rayon, and nylon (*7*). Aqueous emulsions of coconut oil, red oil, and glycerine may be applied to silk or nylon to increase pliability and thus to contribute to more uniform knitting (*35*).

SIZING ——— Glycerine has long been considered a standard ingredient of many sizes used in slashing or finishing. Since the functions of glycerine are essentially the same, whether in slashing sizes or final finishes, both types of operation are hereunder referred to as "sizing." Certain sizes, however, which are employed to produce more highly specialized effects, are discussed under the subheading "B. Special Finishes."

Glycerine promotes the more even distribution and the easier penetration, into yarns, of gelatin, starch, and other sizes. It prevents the drying and hardening of fibers during weaving and subsequent processing, increases fiber workability, and improves the hand of finished goods by its plasticizing action on yarn or fabric. As a result, glycerine is used in various sizes and other finishes to replace or supplement sulfonated oils (*38*) or tallow, both lacking in hygroscopicity. It may also be employed to solubilize or disperse ingredients other than these oils in the sizing bath (*39, 16*).

Sizing compositions that contain glycerine as a plasticizer or lubricant cover a wide range of compounds. Thus, there are formulations based on starches, on proteinaceous materials, such as casein or albumin, and on Tragon, rosin, or combinations of soybean glue and cellulose ethers (*35, 40*). In addition to these and others there are versatile new recipes, applicable to many types of fibers, in which the sizing ingredient is PMA, or polymethacrylic acid (*41, 42*).

Rayon. Many references describe glycerine as a highly valued component of rayon warp sizings. For instance, a report made sixteen years ago by the U S Institute for Textile Research emphasizes the importance of a good softener to the quality of the size itself. The report goes on to state that a higher degree of cohesion and better bodying were obtained by the use of glycerine, rather than sulfonated oils, in combination with starches (*18, 29*). As opposed to tallow, glycerine prevents warp ends from adhering to the drying cylinders of the slasher. It also protects fabrics against the stiffening effect of the dry heat to which they are exposed a few times during processing (*39*).

In warp-sizing of spun rayon, glycerine reduces the flaking of size and the breakage of fibers. Its use generally results in fabrics of greater softness, pliancy, and strength (*26*).

The humectant and lubricant qualities of glycerine are especially useful in standard warp sizes containing sulfated oils, gums, and starches or gelatins (*33, 39*). Typical formulas for sizing acetate or viscose rayon may contain glycerine and formaldehyde, in addition to other sizing agents. A German recipe (Ger 705,263) provides for slashing rayon, at a pH of 7.5 to 9.5, with a sizing composition consisting of gelatin, albumin, or casein, a monohydric alcohol having more than 8 carbon atoms, and a hygroscopic agent, such as glycerine, in water (*18*).

A typical sizing compound for 100% viscose rayon staple may be prepared as follows (*29*):

potato starch	50 lb
glycerine	8 lb
caustic soda soln	1 lb
water	100 gal.

Viscose may also be lubricated and sized with newly patented compositions based on polymethacrylic acid. PMA is a water-soluble compound widely used to size synthetic materials. It strengthens and protects filaments and filament bundles but tends to form brittle films requiring the addition of a humectant and plasticizer. Glycerine is suitable for this application (*42*).

Cotton. For reasons similar to those that apply in the case of rayon warps, glycerine is used very frequently in cotton warp sizing (*43*). In many formulations it is also employed as a solvent for substances added to prevent bacterial and mold growth in the size. One such preparation (U S 2,058,962) contains a fungicide, an inhibitor to prevent metal corrosion, and sulfated castor oil. By reducing the surface tension of the solution, glycerine permits these ingredients to penetrate more rapidly into the fibers (*20*).

Cellulose Acetate. Another sizing composition containing a bactericidal and fungicidal agent (Brit 446,404) is used to condition yarns and fabrics of cellulose acetate. The ingredients are 0.25% hexylresorcinol as the preservative, 4% gelatin, 5% solubilized dextrin, 2% glycerine, and 0.5 to 1% olive oil, all in aqueous solution. Five per cent solids, on weight of yarn, is absorbed by the yarn on passage through this bath (*20, 43*).

It is reported elsewhere that acetate staple fibers do not readily absorb sulfated oils and that glycerine may be used as a substitute. Acetate-viscose blends, however, should be treated with a mixture of glycerine and sulfated oils in a ratio corresponding to the percentage composition of the blended yarns (*44*).

The following acetate size contains glycerine to prevent dryness (*35*):

gelatin	45 lb
glycerine	6 lb
water	100 gal.

Polymethacrylic acid sizing and lubricating agents in which glycerine is the plasticizer are suitable for use on cellulose-derived fibers. A typical PMA formulation is shown below (*42*):

PMA	10 g
glycerol	7.5 g
sodium hydroxide	4 g

This solution is mixed and dispersed with a lubricant composition which contains a mixture of 60% sorbitan monolaurate and 40% polyoxyethylene-castor oil (approx 12 ethylene oxide groups per mole of oil).

The resulting final dispersion is dissolved in water to give a solution with 20%-solids content.

Wool. A hygroscopic agent such as glycerine is frequently a constituent of woolen and worsted warp sizings, particularly in a dry atmosphere. Since antiseptic substances form a desirable part of wool sizings (*45*), the solvent qualities of glycerine may again be utilized to incorporate preservatives in the size.

Some insight into the action of glycerine was gained through tests which demonstrated that glycerine in aqueous solution could penetrate wool fibers much more readily than could pure glycerine. By swelling the fiber, the water increased fiber porosity, facilitated the absorption of glycerine, and produced a softening effect on the fiber (*44*).

Glycerine-Tragon mixtures reportedly improve the workability of wool yarns. Yates supplied this typical formulation for sizing soft botany yarns (*27*):

Tragon	6 lb
glycerine	lb
water	50 gal

A German patent dating back to 1926 (Ger 518,195) already includes glycerine as a softener and moisture-retaining agent in various sizing compositions, one of them based on carob-bean gum; glycerine is to keep the size from drying and subsequently dusting out (*27*).

Man-Made Fibers. Glycerine is a component of sizing compositions for a variety of artificial fibers. For instance, compounds containing partially neutralized polymethacrylic acid and glycerine are applicable to fibers drawn or spun from polyamides and vinyl or vinylidene polymers, in addition to older man-made fibers, such as viscose, cellulose derivatives, and protein fibers (*42*).

Nylon. PMA-based sizes to which glycerine is added are thus particularly useful in slashing nylon, whether in the form of continuous-filament warps of raw nylon or of spun nylon yarns (*41, 35*). Glycerine is the plasticizer in these formulations and produces good film strength and abrasion resistance. Such sizes are easy to apply and can be removed by scouring. The following is a formula for sizing heavy-sley taffeta warp (*41*):

PMA	7%
glycerine	5%
water	88%

Sizes containing mixtures of PMA and sodium alginate also render spun

nylon yarns more resistant to abrasion (*35*).

Glass and Vinyl Fibers. Special formulations for sizing and coating glass and vinyl fibers, as well as nylon and rayon, contain glycerine as a plasticizer. This type of size is essentially a mixture of a water-soluble cellulose ester and soybean glue (*35*).

Japanese studies show that glycerine promotes the crystallization of polyvinyl-alcohol fibers by softening such fibers during heat-treatment (*41*).

MISCELLANEOUS SIZING APPLICATIONS———*Felting.* Because of fiber affinity and lubricating capacity, glycerine is a valuable component of sizes used to make felts (*20*). Kapok, for instance, may be dipped or soaked in a hot bath that contains sodium phosphate and a wetting agent; it is thereupon cold-oiled with latex and glycerine and subjected to the usual felting methods (*46*).

Stabilization to Freezing. Glycerine may be used in a special rosin size applicable to paper or textile fabrics (U S 2,268,112) for the purpose of stabilizing sizing dispersions against coagulation on repeated freezing. The other basic ingredients of this size are rosin soap, free rosin, and a protective colloid (*18*).

Softening Action. Degraded-cellulose ether sizes or fillers are applied to textiles or other fibrous substances from a bath that contains glycerine (U S 2,442,572). Sizes of this type give permanent results without harshening or stiffening the fiber (*47*).

FINAL FINISHING———By virtue of its lubricating and moisture-stabilizing action on textile fibers, glycerine serves as a valuable softener and plasticizer in many final-finishing operations. In his extensive coverage of the technology of textiles, Diserens described glycerine as "certainly the most important hygroscopic agent used in finishing" (*38*).

The difference between a softener and a plasticizer has been clearly stated by Valko in these words: "A plasticizer is a compound which reduces the elastic modulus of resins, rubber or other polymer materials by facilitating the movement of the polymeric molecules in the plastic body. A plasticizer is an internal lubricant for molecules, whereas a textile softener is a mere surface lubricant." With respect to the two-fold effect of a softening agent on the bending of a fiber bundle, Valko continued: "First, individual fibers bend and this involves stretching and sliding upon each other. Evidently, the easier the fiber slides, the easier it is to bend the bundle, that is to make it softer. An internal plasticizer would make the individual fibers easier to bend, but fats and oils do not penetrate fibers sufficiently to act that way" (*48*).

In a personal communication to the authors, Valko classed cyclic nonionic surfactants with fats and oils as compounds which are solely surface lubricants (*49*). He expressed the view that the thickness of the cyclic component prevents the molecules of such compounds from penetrating between the molecular chains of textile fibers, whereas the glycerine molecule is small enough to act as a true plasticizer. As evidence Valko cited the effect obtained from experiments on the swelling of wool fibers and human hair (see *44*).

Softening and Plasticizing Action. Examples of this action include the use of glycerine to treat rayon that has lost its natural softness during finishing (*26*), to prevent wool felting and shrinkage due to the evaporation of hygroscopic moisture during dry weather (*27, 37, 50*), and to produce a softening effect on cotton lawn impregnated with an organdie finish (*51*). In the latter application glycerine is incorporated into the finish in the following proportion (Brit 573, 574):

	parts
polyvinyl alcohol	25
glycerine	5
formaldehyde	5
ethylene chlorohydrin	1

A cotton finish based on starch and glycerine is applied to dyed goods after drying (*10*).

Research on lac in India has shown that glycerine is an effective plasticizing and solubilizing aid in coating compositions and finishes. For instance, cotton used to make oil cloth may be coated with a varnish colored with kaolin and containing 20 parts of glycerine to 100 parts lac, 40 parts linseed-oil fatty acids, and 8 parts ammonia (*51*).

Ropes for use in aviation or other mechanical apparatus, conditioned to withstand shock, heat, or rough weather, may be made by immersing undrawn synthetic fibers of, eg, the polyamide, polyester, or vinyl type, for 24 hours in a solution containing 80% shellac, 10% glycerine, and 10% pitch solution (⅓ pitch and ⅔ methanol). The plastic fibers retain about 20% by weight of this composition (*51*).

The following formulation may be used to finish heavy woolen cloth (*27*):

water	15 gal
potato starch	3¾ lb
Lupogum	6 oz
Glauber's salt	3½ lb
magnesium sulfate	3½ lb
glycerine	10 oz.

Among glycerine derivatives used in textile finishing, an alcohol-glycerine condensate is particularly useful as a solvent or softening agent for cellulosic-fiber threads and filaments (*43*). Some polyglycerides have been proposed as softening and conditioning aids for various types of fabrics (*7*).

The importance of glycerides as intermediates for textile-finishing assistants has greatly increased during recent years as a result of improved techniques for their utilization and of a greater need for lubricants and softeners stable under high-temperature conditions. For example, hydrogenated glycerides with very low iodine numbers are nowadays obtainable at relatively low cost and may be reacted directly with alcohols or amines to give highly refined fatty-acid esters or amides without need for prior hydrolysis and purification. These fully hydrogenated glycerides themselves show great stability to heat discoloration, a property important in modern textile finishing. A typical example of high temperatures encountered in finishing is the high-speed application of urea-formaldehyde or melamine-formaldehyde resins to cotton or rayon fabrics for reproducing the "drip-and-wear" characteristics of synthetic textile materials. These resins also require a considerable admixture of softener to keep the fibers from becoming harsh and brittle. Very rapid sewing sometimes necessitates lubrication of the fabric, not just the thread, as the needles become so hot that there is danger of cutting the fabric or of melting thermoplastic fibers (*48*).

Weighting. Preparations used to weight fabrics frequently contain glycerine as the hygroscopic component. Thus, Fr 825,474 advocates the use of glycerine in weighting processes to give fabrics a better hand and increased elasticity (*46*); Ger 731,971 proposes the addition of glycerine to water-soluble meta- and polyphosphates to improve their weighting effect (*28*). Bennett, in Volume VI of "The Chemical Formulary" (1943), lists this composition for weighting textiles (*26a*):

	parts
glycerine	6.0
urea	2.0
potato starch	2.0
sodium benzoate	0.2
water	27.8

B. Special Finishes

Many highly specialized finishes contain glycerine as a hygroscopic agent, plasticizer, solvent, or gas-

resistant substance. It is used in these and similar capacities to counteract static electricity on the fiber, to increase flame resistance as well as water repellency in many types of fabrics, to produce scroop on cotton, to control the rustling of rayon, and to prevent the shrinkage and felting of wool. Other special treatments for textiles include crimping and anticrease processing, delustering, gasproofing, nylon whitening, and producing resistance to mildew. Resinous coatings, in which glycerine is frequently both an ingredient of the resin and an additive thereto, will be described separately under "Resin Finishes" in a future paper.

ANTISTATIC TREATMENTS——Glycerine, as the hygroscopic component of antistatic finishes, absorbs moisture onto electrostatically charged fibers or fabrics. It thereby increases the conductivity of such materials and produces a discharge of electricity along their surface or through the fabric (*52, 53*). Esters of glycerine may serve the same purpose (*54, 55*). Because surface charges present a serious problem to the manufacturer, and, at best, a nuisance to the wearer (*53*), the elimination of static electricity is important to both. Cellulose-derived fabrics and the newer synthetic textiles tend particularly to accumulate static; however, silk, wool, and rubberized fibers may behave similarly.

Cellulosic Esters and Ethers. In the weaving of yarns of cellulose acetate or of other cellulosic derivatives on certain types of looms, curling of the weft occurs as a result of electrification. According to a Celanese patent, this may be rectified by applying to the yarn a hydroxy alkylamine and/or a suitable derivative thereof, such as a reaction product of the amine with one of the higher fatty acid esters of glycerine; the ester should contain at least one free hydroxyl group, as, eg, glyceryl mono- or dioleate or palmitate. These antistatic agents are employed alone or with water or organic solvents. If the finish is applied from such a solution or suspension, glycerine may be used as an additive (*54*).

Another patent granted to the same company mentions glycerine as a hygroscopic agent suitable for dissolving up to 50% of the proposed antistatic compound, an aliphatic diamine salt of a hydroxycarboxylic or other acid. Even 0.5% owf of this diamine salt is reported to be completely effective in de-electrifying and flexibilizing cellulosic yarns in textile processing; 0.5 to 1% is recommended for previously untreated fabrics; and 2 to 5% is considered adequate for treating the yarn so that the effect carries into the fabric. However, if a lubricant, such as glycerine, is used along with the finish, the patent claims that 0.1% of the antistatic diamine salt is sufficient (*56*).

Synthetic Fibers. Static electricity interferes with the "winding, throwing, warping, and pirning" of yarns consisting of filaments of synthetic linear polymers (*57*). Yarns with low electrical conductivity and with a low regain of moisture, such as yarns of polyhexamethylene adipamide (nylon 66), are particularly prone to untwisting as a result of electrostatic repulsion. Brit 649,877 claims the prevention of the untwisting of yarn, the subsequent ballooning of filaments, and even the breakage of thread by treatment of the yarns with a solution of sodium chloride in aqueous diethylene glycol or glycerine. The aqueous solution should preferably contain 15 to 25% by volume of water (*57*).

Brit 747,827 claims that a highly effective antistatic finish for nylon and Terylene (same as Dacron) polyester fiber is obtained by dissolving an organic polyisocyanate and a polyethylene glycol in ethyl acetate. The polyisocyanate may be prepared by treating 200 parts of toluylene 2:4 diisocyanate above 80°C with 23 parts of glycerine and 21.2 parts diethylene glycol in 81.4 parts of ethyl acetate. Nylon and Terylene are immersed in this solution, drained after ten minutes, and baked for fifty minutes at 120°C (*58*).

Miscellaneous Fibers. In the manufacture of rubberized threads and filaments, the generation of dangerous static charges is prevented by the use of antistatic preparations containing glycerine (*43*). Silk and rayon may be protected from electrification by immersion and soaking in baths to which glycerine has been added (*46*). The elimination of static in the carding room when glycerine is used in the oiling of wool has already been mentioned in connection with sizing and lubrication (*29*). A new method for treating drycleaned fabrics and clothing consists in aftertreating the goods with a solvent containing 0.02 to 5% of an antistatic agent, such as, eg, glyceryl monooleate (*55*).

FLAME RESISTANCE—Glycerine is useful as a humectant and plasticizer in many types of fire-retardant finishes. One such compound is the reaction product of an aluminum salt, ammonia, and glycerine. Fabrics finished with this compound may be subjected to further treatments that will produce water repellency as well (*44*). Another composition is a special soap prepared by mixing 180 parts of a dry-powdered soap with 24 parts of sodium silicate and by making this mixture into a dry paste through the addition of 8 parts potassium carbonate, 7 parts glycerine, and 4 parts sodium tungstate. Cotton washed with this soap is rendered nonflammable (*25*).

A resinous fire-retardant finish, which is also a sizing agent, lubricant, and adhesive softening agent used in combination with amine resins to shrinkproof cellulosic fibers, is obtained by adding triethanolamine to glycerine condensed with boric acid and borax (*12, 35*). The use of glycerine in a borophosphate resin reduces the loss of flame-resistant agent on exposure (*12*).

Among the numerous flame-resistant finishes based on phosphates is a composition for use on cellulosic textiles and paper. It is made by reacting a hydrogen-containing oxide of a phosphorus compound, such as diammonium phosphate or phosphoric acid; a dibasic acid amide, such as urea; and a polyhydric alcohol with hygroscopic properties, eg, glycerine. This composition acts also as a softener (*59*).

The following treatment produces suitable substitutes for asbestos cloth and reduces the afterglow in fabrics (*12, 60*):

Cloth is saturated with a solution of 2 lb diammonium phosphate in 1 gal warm water, dried, and then coated three times with a mixture of

	parts
casein	100
water	400
glycerine	130
ammonia soln, 25%	10

The finished fabric may be used for heavy-duty welding curtains, tents, and like articles of military or industrial significance.

Chlorinated rubber modified with glyceryl borate has similar applications. Cotton bases impregnated with this finish, which also depresses afterglow, may be made into flame-resistant, flexible awnings and curtains (*12*).

WATER REPELLENCY — The plasticizing action of glycerine appears to be its most important attribute in water-repellent finishes and coatings. Glycerine prevents excessive brittleness of the impregnated fabric and maintains the pliability of the coating itself. For example, glycerine was used in an early British patent (469,932; 1937) as a plasticizer for a water-resistant, stiffened finish on textile fabrics, such as linen or silk (*43*). A Jap-

anese patent (131,411; 1939) claims a latex composition containing a large proportion of glycerine for the waterproofing of cloth (*32*).

Tent materials, such as canvas or drill, may be waterproofed with coatings of insolubilized gelatin to which glycerine has been added as a plasticizer (*12*). A typical treatment for tent cloth consists of two solutions, viz:

I	*parts*	and	*II*	*parts*
light glue	10		formalin	100
water	50		water	900
glycerine	10			

Solution I is applied to both sides of the fabric and allowed to dry; solution II is used as a hardening bath (*25*). Earlier methods were based on the use of chromated gelatin solutions, and more recent ones, on gelatin films insolubilized by tannin; in either case, approximately 10% of glycerine was employed (*25*).

A Canadian patent (387,351; 1940) describes a special varnish for making textile surfaces water-repellent. A formulation applicable to table cloths and aprons is prepared as follows (*25, 44*):

	oz
linseed oil, refined	4
camphorated turpentine	4
kerosene	6
castor	4
glycerine	2
China wood oil	1

Zein, a vegetable protein derived from corn, is best known in the textile field as the raw material for Vicara fiber (*53*). However, a comprehensive annotated bibliography on the product shows it to have many other uses besides. Thus, US 2,047,961 describes how zein may be transformed into a highly water-resistant substance, suitable for impregnating films and coatings. This is done by reacting the zein in a water-alcohol solution with formaldehyde in the presence of glycerine as a plasticizer. Then, an alcohol-soluble phenol-formaldehyde resin as well as hardeners and plasticizing agents for the resin are added (*61*).

RESISTANCE TO POISON GAS—In 1937 news came from Holland that glycerine and glycerine-gelatin mixtures ranked high among several substances found to be practically impermeable to mustard gas (*25*). This discovery, by Klarenbeek, was soon followed by a Dutch patent (47,000; 1939) for treating cotton to withstand mustard gas. According to the patent, one side of the fabric is given a rubber coating and is then vulcanized; the other side is impregnated with 90 parts of a 35% water solution of gum arabic and 10 parts of glycerine (*25*). In another Dutch patent (49,367; 1940) glycerine was used to soften a textile-impregnating coating based on cellulose acetate, which is partially saponified in the course of the treatment. The addition of a latex layer is optional (*25*).

Additional work done in this country yielded several applications useful during World War II. For instance, the idea that a glycerine-containing substance, cellophane, might provide protection against war gases led to the use, by some of our troops, of cellophane capes plasticized with glycerine (*44, 62*). Katz reported in 1943 that adhesives of glycerine-plasticized gelatin could be employed in laminating cloth for the production of gas-resistant tarpaulins and similar fabrics. The gelatin-glycerine mixture had to be insolubilized with chromates or formaldehyde (*62*). Where the mixture formed the inner layer between laminations, glue might replace the gelatin. The use of tarpaulins treated in this fashion was suggested for the protection of foodstuffs from poison gases, such as mustard or lewisite (*12, 26a*). In addition, glycerine is incorporated into miscellaneous gasproofing finishes, such as a nylon coating (*12*).

Glycerine may also be used in a composition to prevent the escape of dangerous ethylene oxide vapors from equipment employed in the application of a special cotton finish. This composition consists of equal parts of glycerine, gelatin, and sugar, dissolved in warm water and allowed to cool and set into a thick, nondrying jelly (*44*).

CRISP FINISHES——Less spectacular than gasproofing but of immense every-day importance are textile treatments which impart a desirable hand to fabrics. An award-winning study in this field was published in 1953 by Nuessle and Crawford (*63, 64*), who found that an unusually durable, crisp, and washfast finish on nylon can be obtained by heat-setting polyacrylic acid (PAA) onto nylon in the presence of glycerine. Although PAA alone reacts with the surface molecules of nylon, carboxyl groups that remain unreacted cause excess acidity. When this acidity is neutralized before application to nylon, the durability of the finish is impaired. This difficulty is readily overcome by coreacting glycerine with the PAA during the application. Of the many coreactants tried with PAA, glycerine proved to be the most effective with regard to "crispness, durability, and freedom from discoloration." It also seemed to function as a "solvent medium" which facilitated the reaction between PAA and nylon (*64*).

It was further discovered that a very stiff finish, which becomes even more pronounced on washing, may be obtained with glycerine alone under severe curing conditions. This finish is too brittle for practical use, whereas the PAA-glycerine finish finds commercial application, particularly for stiffening nylon lace. However, the glycerine-nylon experiment showed that a reaction takes place between these two materials, a discovery confirmed in other work published the following year (see *23, 23a*).

The invention of Nuessle and Crawford was patented in 1954 as a method for producing a stiff, durable finish on nylon (*65*). The patent prescribes the use of an aqueous solution of polyacrylic acid and a polyhydric alcohol, the optimum ratio by weight of acid to alcohol varying from 10:2 to 10:5. The most favorable molecular-weight range of the PAA is defined in terms of viscosity; the polyhydric alcohol is to possess less than six hydroxyl groups per molecule and may be glycerine or polyglycerine. The finish, which contains 1 to 10% PAA on weight of nylon, is applied from the bath by padding, dipping, or by other means at temperatures ranging from 300 to 425° F; the treated fabric or yarn is thereupon dried and heated from ten seconds to one hour. The cure insolubilizes the finish on the nylon and renders it extremely fast to repeated washings, even at high temperatures (120 to 160°F) and under conditions of mild alkalinity. Typical sample formulations contain, for instance, 1% glycerine and 3% PAA, to stiffen a nylon taffeta; 2% glycerine and 10% PAA, for padding a dyed nylon marquisette; and 3% polyglycerine plus 5% PAA, for a sheer nylon fabric.

Older processes using glycerine in crisp finishes include a formulation and method of application shown in Bennett's "Chemical Formulary" (1945) for giving more scroop to cotton materials (*60*). This composition is made up as follows:

	parts
magnesium chloride	15.0
magnesium sulfate	20.0
glycerine	5.0
corn syrup	42.0
formaldehyde	0.2
water	17.8

Conversely, glycerine is also useful in an analytical method for controlling the rustle of fabrics. When rayon is treated with resins to decrease rustling, the point at which the resins are evenly distributed and have attained the desired small particle size can be checked by means of Hohnel's reagent, a solution of sulfuric acid, potassium iodide, and glycerine (*43*).

WRINKLE FINISHES—Glycerine is an old stand-by in compositions for the crimping of fabrics. For instance, a British process consists in crimping cellulose-derived organic fibers by shrinkage with a finish containing an aliphatic aldehyde, such as acetaldehyde, water, and a compound containing hydroxyl groups, such as glycerine (*18*). Similarly, an American method is based on treating fibers of cellulose acetate or of other cellulose esters with an ester of glycerine. Fibers thus treated yield fabrics resembling wool in retention of crimp and elasticity during ordinary use (*32*).

A new type of wrinkle-drying coating is formulated with an organic solvent, a terpolymer of vinyl chloride, vinyl acetate, and vinyl alcohol, and a resin prepared by cooking either one of the following mixtures (*66*):

	% by weight	
	A	*B*
glycerine	19.0	12.28
phthalic anhydride	38.0	19.93
linseed-oil acids	21.5	16.94
tung oil	21.5	26.58
maleic anhydride	—	1.15
resin	—	23.12
total	100.0	100.00

CREASE RESISTANCE—Resin-free anticrease treatments frequently employ glycerine as a means of protecting the fiber against harshness or brittleness produced by the finish (*33, 46*). In finishes comprising solutions or dispersions of borates, stannates, or silicates, glycerine serves as a plasticizing agent (*29, 33*). It is likewise added to finishes for making cellulosic textiles crease-resistant by the formation or deposition of a metal compound in the fiber structure. One such finish, which consists of a 5% calcium acetate solution plus 1% glycerine, is applied to rayon fabrics freed from sizing materials. The fabric is then squeezed, dried, and impregnated again, this time with a 5 to 10% sodium silicate solution containing 0.5 to 1% glycerine. Heat treatment at 100 to 150°C completes the operation (*43, 62*). Glycerine-dialdehyde solutions (*33*) and glycerine derivatives generally used as surfactants (*7*) have also found application in processes for rendering textiles crease-resistant.

LUSTERING AND DELUSTERING——Occasionally, glycerine is used to impart luster to fabrics, as in the case of acetate fabrics delustered slightly by dyeing and finishing at very high temperatures. Treatment of such goods with an aqueous alcohol solution containing a small quantity of glycerine usually restores their luster (*13, 29*). Glycerine may also be employed to produce gloss on certain woolen fabrics (*39*).

More often, however, glycerine is incorporated into finishes designed to deluster rayon and other fibers. For instance, the inclusion of glycerine in rayon-delustering finishes based on tin compounds aids in the uniform precipitation of barium stannate. One bath, instead of two, is therefore sufficient. The even dullness effected by this method can also be produced on other staple fibers and mixed fibers (*67*).

According to another process, rayon is delustered by the use of aqueous pigment dispersions. The dispersing agent is a polyglycerine ester (*68*). Another glycerine derivative, triacetin, may be used as one of the organic swelling agents or cellulose-ester solvents suitable for rayon delustering when applied in the form of a paste or solution. Examples of such pastes contain titanium dioxide, glycerine, formic and acetic acid, and gums. They produce a dull, washfast finish on cellulose ester yarns or fabrics (*69*).

CONTROL OF SHRINKAGE——Two Australians, Freney and Lipson, worked out a three-bath treatment for preventing or minimizing the shrinkage or felting of wool. In this method, 1% glycerine is used in the first bath to inhibit discoloration; the basic ingredient is a 7% potassium hydroxide solution in 95% ethyl alcohol. The second bath effects neutralization by means of dilute sulfuric acid, and the third is a rinse with flowing water (*27, 62*). Variations of this method also include the use of glycerine, since a dark-brown color develops without it (*62*). Other treatments to reduce wool shrinkage (eg, Fr 807,021 and Brit 475,422) likewise employ glycerine in the bath. A typical formulation is as follows (*27*):

	parts
formaldehyde (38–40%)	19
boric acid	4
glycerine	3
urea	10
water	95

This solution reacts with wool fibers, yarns, or fabrics to yield a nonresinous amino condensation product. In addition to an antishrinkage effect and other advantageous properties imparted to wool, solutions of this kind make wool more resistant to oxidation and to moths. A treatment for heavy woolen cloth is another instance of the incorporation of glycerine in a wool finish (*27*).

Similarly to woolen fabrics, woven or knitted textiles made of cellulosic fibers may also be protected against shrinkage by means of an alkali solution containing glycerine (*43*). Vegetable or animal fibers in the form of loose, carded webs may be impregnated with a rubber-latex base containing ammonia, gelatin, and glycerine. This finish produces unshrinkable, waterproof fabrics (*43*).

RESISTANCE TO HARMFUL MICRO-ORGANISMS——According to a German patent (672,116), fibrous materials may be protected against damage by molds and by bacteria causing rot by treatment with complex copper compounds. The latter may be prepared by reacting glycerine with a copper salt in the presence of a caustic solution (*25, 46*).

MISCELLANEOUS FINISHES——Many other finishing recipes utilize glycerine for a variety of purposes. For instance, Soviet plants used to employ four kinds of finishes prior to 1944. Eventually, the Central Scientific Textile Institute produced a single standard finish that was to be effective as well as inexpensive. It consists of vegetable oil, Turkey red oil, animal glue, stearin, starch, fats, glycerine, calcium chloride, and water (*9*).

A fairly recent invention comprises a new type of wash-and-rinse composition for whitening and brightening nylon goods, particularly hosiery, clothing, and other textile articles used in the home. These compositions, which prevent the development of a yellowish cast and the off-white, dull appearance frequently caused by light, laundering, etc, are greatly improved by the addition of a hygroscopic agent, such as glycerine. The patent states that the polyhydric alcohol aids in eliminating the build-up of electrostatic charges in the rinsed and dried nylon goods. Six out of the 19 specific rinse compositions shown do indeed contain glycerine. A general formula illustrating these compositions has the following ingredients (*70*):

p-dimethylamino-beta-methylcumarin (or p-diethylaminocumarin)	1½ oz
tert-butyl alcohol (or ethyl, methyl, or isopropyl alcohol)	3 lb
sulfuric acid (optional) (or hydrochloric acid)	1½ oz
glycerine	1½ oz
water	balance to yield 8 lb.

NONRESINOUS COATINGS——Coatings differ from other finishes in that they are usually thicker and in that they form a continuous surface over fabrics, producing a change in structure. According to Mauersberger, fabric coating is a highly specialized field in which the coater usually does not carry out any other textile operation (*53*).

Glycerine is frequently used as a plasticizing agent to increase the flexibility of coatings (*10, 33*). A

typical example is a flexible, gasolineproof fabric made by coating a sateen base with a composition containing glue, water, sorbitol, and glycerine (Brit 495,352). Heating the fabric and insolubilizing the coating by washing with an aqueous formaldehyde solution completes the treatment (*33, 46*). Some coatings benefit from the insolubility of glycerine in many oils and organic solvents (*33*). For instance, glycerine is an ingredient of several cloth coatings resistant to oil, grease, and hydrocarbons (*10*).

Originally, coatings were applied only to cotton fabrics. Later they were also used on rayon, nylon, and even glass-fiber textiles (*53*). A US patent for preparing semi-transparent, coated nylon fabrics resistant to solvents, alkalis, acids, and hot or cold detergent solutions was granted in 1954 (*71*). The method consists in passing nylon through a solution of 22 parts butyl acetate, 16.5 parts ethyl acetate, 16.5 parts benzene, 11.25 parts 2,4-tolylene diisocyanate, and 45 parts polyester solution; in draining the fabric; and in heating at 100° C for 35 minutes. The polyester solution (a pale-yellow liquid of 200-poise viscosity and 6% hydroxyl content) is prepared by stirring the following ingredients for 4½ to 8½ hours at 200°C in an atmosphere of carbon dioxide:

	parts
glycerine	430
ethylene glycol	917
adipic acid	2000

It is claimed that nylon fabrics obtained in this manner have a pleasant hand and drape. Creasing does not mar or crack them, and wrinkles are easily removed by ironing.

Nylon may itself serve as a coating material when used in the form of a fine powder in suspension. Linear polyamides (nylons) are convertible into such powders by solution at an elevated temperature in a polyhydroxy compound, such as glycerine, followed by the removal of foreign matter and the subsequent precipitation of the nylon by cooling. The temperature required for completely dissolving, eg, polyhexamethylene adipamide, in glycerine is 188°C; for polyhexamethylene sebacamide in glycerine, 183°C (*72*).

Zein, too, makes a suitable ingredient for coating materials. For this purpose it may be dissolved in an alcohol of low molecular weight, such as ethanol. The resultant solution is stabilized and the zein film is caused to turn white on drying by the addition of alcohol-soluble opacifying agents, such as chloroethyl ether, cyclohexanol, or glycerine. Coatings thus prepared repel oil as well as moisture and provide an excellent base for printing (*61*).

A recently reported adhesive and coating for fibers, threads, and textile materials has this composition (*73*):

	%
carboxymethylcellulose	6
glycerine	2
sodium alkylarylsulfonate	2
sodium hexametaphosphate	1
water	69
alcohol	20
total	100

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NEW ASPECTS OF THE PAD-ROLL SYSTEM*

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APPLICATIONS

DYEING——The Pad-Roll system for dyeing with substantive dyestuffs has been widely accepted. This is generally due to the exceptional economies obtained, but in addition the system has proved to be an excellent one when used in the preparation of fabrics for dyeing.

Much has already been published about the principle of the Pad-Roll dyeing range (*1, 2, 3, 4*), but it is perhaps not out of place here to describe the process again in outline.

Although many of the substantive dyestuffs or, as these are usually called, direct dyestuffs, in light to medium shades can be fixed on the surface and the outer layers of the fiber by aging of the padded fabric or by means of a salt bath, the optimum wetfastness generally cannot be obtained. In order to achieve the optimum fastness properties, one must be sure that the molecules of a dyestuff diffuse into the innermost fibers in such a way that distribution is even throughout the entire cross section of the fiber and complete equilibrium must exist. The diffusion is a slow process and dyeing-in times of from one to six hours are necessary, depending on the depth of shade, to allow the system to obtain equilibrium. In order to accomplish this, it is necessary to keep the dye-impregnated fabric at the predetermined dyeing-in temperature and humidity for the time necessary to obtain this balanced dyeing-in.

These conditions, which constitute the ideal situation, are being achieved by the Pad-Roll machine. (See Figure 1).

The goods are first impregnated on a padder and evenly squeezed. The padder is equipped with a special pan allowing for a comparatively long passage of the goods. But the pan is also equipped with a removable insert which can be used to reduce the liquor volume to a minimum.

The relatively long passage is necessary in order to allow the fabric to swell completely before squeezing, so that any variations in the operating speed have the minimum effect on pick-up. The smallest possible liquor volume is also necessary in order to prevent substantivity effects. These substantivity effects are further reduced to a minimum in the lighter shades by padding with dyestuffs having pronounced substantivity at low temperatures. Inasmuch as it is undesirable in most cases for the diffusion of the dyestuffs during the later fixation to have a high electrolyte concentration, it is recommended that concentrated dyestuffs be used, thus further diminishing or eliminating substantivity effects. It is also beneficial to fill the padder pan slowly when the machine is being started and to use high operational speeds. After the impregnation and squeezing, the fabric passes a compensator and is led through a narrow slot into a horizontal heating zone, where it is treated on both sides with infrared rays and heated to the desired temperature. Immediately connected to the infrared heating zone is a transportable batching chamber into which the fabric passes after heating, and here it is batched on a large diameter batch roll. This carefully insulated chamber is preheated by means of electrical heating elements and filled with saturated steam until a wet-bulb temperature corresponding to the desired dyeing-in temperature is attained. Wet- and dry-bulb temperatures are set automatically by means of controlling instruments. Here the dry-bulb temperature is set a little higher than the wet-bulb temperature, thereby eliminating any condensation inside the chamber. In order to avoid condensation drips, the ceiling of the chamber is heated.

It follows that the fabric can be heated in the infrared zone till it reaches a temperature equivalent to the wet temperature inside the chamber. The infrared zone is regulated in such a way that the wet temperature remains constant or increases slowly a few degrees. By keeping the wet temperature constant, one can be sure that the fabric is being batched from start to end at the same temperature. The surrounding atmosphere, which for all practical purposes in saturated, prevents evaporation and therefore any consequent change in the dye concentration within the batch. After the batching is completed, the entire dye lot is rolled up in the chamber,

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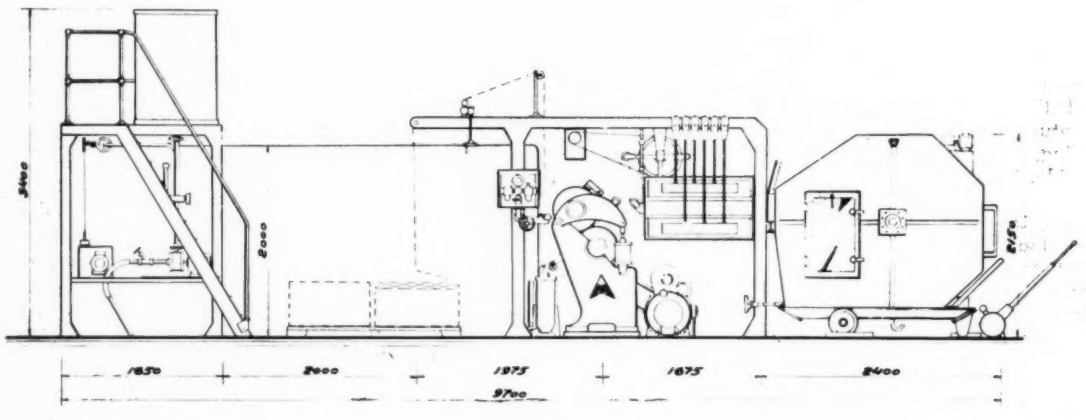

Figure 1
Svetema Pad-Roll Dyeing Machine

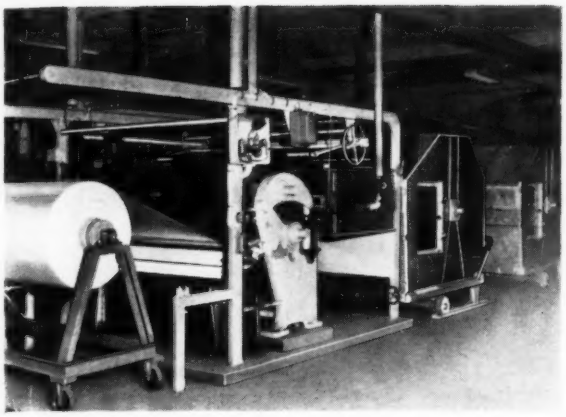

Figure 2

Figure 3

the chamber is separated from the infrared zone and moved to a storage position. The chamber at this stage is completely closed. The fabric on the slowly rotating batch roll is kept in the chamber for the time necessary to achieve the complete indiffusion of the dyestuff under fully controlled and predetermined atmospheric conditions. After separation of the full chamber from the infrared zone, a new chamber is connected and a new dye lot can be started. By using three to four chambers, it is possible to achieve an operation which for all practical purposes is continuous. As it is possible to dye two or more shades on one batch roll, the Pad-Roll dyeing system is also most economical for comparatively small lots.

The tension is regulated by the previously mentioned compensator, which governs the batch drive, and can be set by means of a sliding weight to any desirable tension from 200—4000 grams. The compensator further serves to create a path between the padder and the infrared zone for a certain cooling-off of the fabric.

In the padding of fabrics which have a tendency to swell to a large degree, and especially in the processing of heavier types of spun rayon fabrics, it is evident that the goods leave the padder nip while unfixed dyestuff is concentrated more in the inner fabric rather than on the surface of it. This is especially so when heavier shades are concerned. Inasmuch as a spun rayon fabric having low dyestuff affinity is padded mostly at high temperatures, the evaporation caused by the cooling space results in a migration of the dyestuff molecules back to the surface of the fibers. Naturally this cooling-off must not be overdone so that the dyestuff does not precipitate. It would be extremely dangerous if the fabric were cooled-off in the nip itself to such a degree that the precipitation would take place there. In that case the migration of the dyestuff back to the surface naturally would be blocked in a way and the best visual effect could not be expected. For this reason the goods are led through the nip of the padder tangentially and it might possibly be desirable to preheat the padder bowls.

It further seems probable that, during this cooling off, a certain superficial fixation of the dyestuff takes place, which together with the reduction of the moisture content in the fabric causes a retarding of the migration of the dyestuff so that the evenness of the dyeing is furthered if affinity differences in the material exist.

In the padding of spun rayon goods, differences in moisture content of the goods to be dyed are extremely noticable with respect to the optical shade values. Experience has shown that optical color values can be lessened by 30 to 50 percent if the fabrics to be dyed have a moisture content of from 11 to 12 percent as compared to fabrics having only 3 to 4 percent moisture content. It is therefore recommended that the goods be overdried after the pretreatment and kept in a very dry room before the dye impregnation. It is further recommended that the Pad-Roll dyeing machine be kept in a dry room.

Figures 2 and 3 show two views of a Pad-Roll dyeing installation.

DESIZING———In order to obtain best results in the dyeing of fabrics it is necessary to prepare the goods most carefully for the Pad-Roll dyeing system, just as such a careful preparation is necessary for all other padder continuous dyeing systems.

No matter which type of goods are to be dyed, be it cotton, viscose, acetate or even nylon, a complete desizing of the fabric is of more importance than is commonly known. Even with conventional dyeing methods, such as beck or jig, goods that are desized unevenly will cause many complications, which are sometimes attributed to other factors. The desizing can be fully accomplished only with economical application of chemicals under exactly controlled temperatures. These conditions prevail in the Pad-Roll System. If the desizing is incomplete, and thus in most cases also uneven, the wettability of the goods in the succeeding dyeing process is also uneven, which means that the indiffusion of the dyestuff can be impeded. In many cases where shortcomings of dye properties were attributed to differences in affinity of the fabric, it has been proved that the actual cause was incomplete desizing.

If, on a Pad-Roll machine, a bacteriological desizing agent is used, which has its maximum activity at temperatures of from 75—80° C, a complete desizing takes place within twenty minutes of the last end of the goods entering the chamber. If the material consists of regenerated cellulose, a complete swelling of the goods is achieved at the same time, so that many times no further pretreatment is necessary except for a careful rinsing before drying with as little tension as possible.

In the case of a water-soluble size, it is advantageous to dissolve the size on the Pad-Roll machine and to swell the fabric at the same time, which can be done just as fast. The size thus can be rinsed off very easily. If the goods are gelatin-sized and are to be bleached, the desizing and bleaching with sodium chlorite

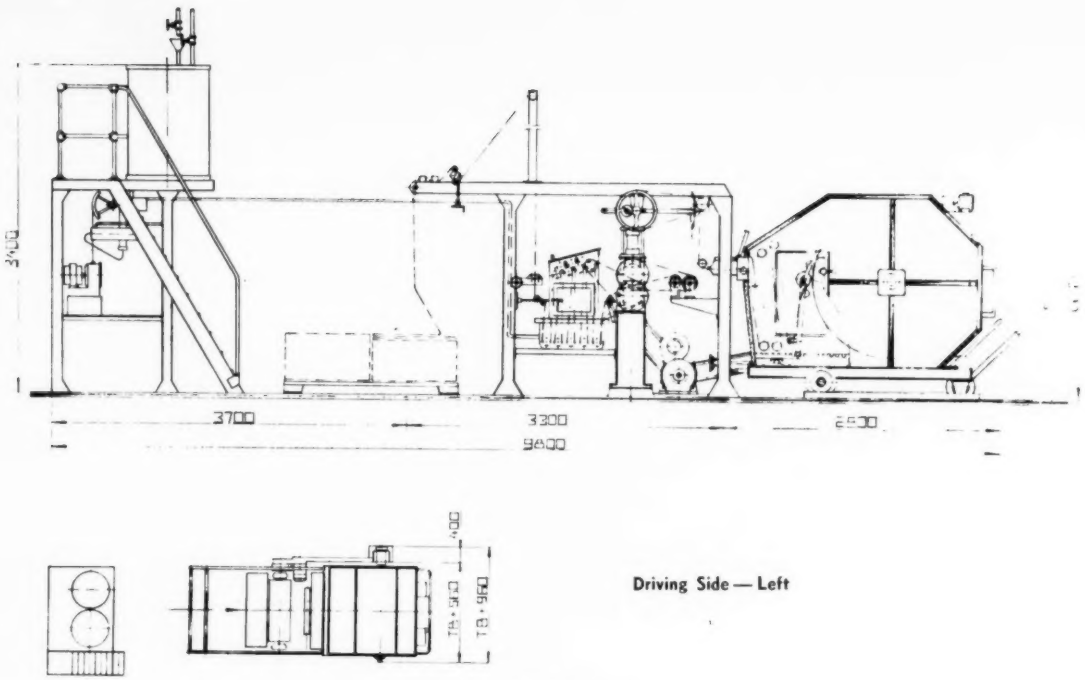

Figure 4
Pad-Roll Bleaching Machine

can be done in one process.

It could be argued here that a Pad-Roll machine is too expensive an installation to be used for desizing.

It has been stated, however, that the machine in practice proves to be very economical, especially in view of the evenness achieved and the fact that even the most delicate fabrics can be handled. In one case, a mill that mainly handles heavy spun rayon goods received a Pad-Roll range in the middle of the season, and therefore it was impossible to employ the machine immediately for the dyeing process. In order to utilize the installation immediately, it was decided to use the machine for desizing. The improvements in the beck dyeing were so surprisingly high that the machine was immediately operated on a three-shift basis for desizing only. Poor dyeing, which had been frequent due to incomplete desizing of heavy goods, was almost eliminated, and due to the perfect preswelling of the goods almost no creases appeared. Since the pretreatment was always completely even, less color matching was necessary, and above all, the productive capacity of the beck dyeing unit was increased. This mill now desizes all goods on the Pad-Roll machine, whether large or small lots are processed. It was said that the Pad-Roll machine, for the above-mentioned reasons, has paid for itself within a very short time. In addition there was a quite a considerable saving on desizing agents.

It is worth while to point out here that it is more important to achieve even and complete desizing and consequently even dyeing when plain acetates and nylon constructions are involved than with any other type of fabrics.

BOILING-OFF——The Pad-Roll machine is also well suited for the boiling-off of cotton fabrics with alkalies. In this case, the goods are padded at a high temperature, using about 25 to 30 grams of sodium hydroxide and four to five grams of a suitable detergent per kg of fabric. Temperature is left constant at about 95° C for approximately two hours in the chamber. The boiling-off process is then executed in such a manner that the goods are evenly treated from end to end for highest possible wettability. This particular pretreatment, including the desizing, will prepare the goods excellently for the following pad-dyeing process. If goods have to be bleached in full width, the Pad-Roll system also provides an excellent method of treatment.

Although the desizing and treatment with alkalies can be easily accomplished on the normal Pad-Roll range, a special construction of the impregnating arrangement and of the transportable chambers is recommended.

In case only desizing or alkali treatment are to be executed, and in which case the impregnation will be made hot, the chambers can be executed much simpler and cheaper than the normal dyeing chambers. Low cloth tension in batching, however, is still most essential and the special batch drive is necessary.

BLEACHING——If the range is to be used for bleaching, both a special impregnation unit and a special construction of the chambers is essential. On the other hand, the chambers which are especially built for bleaching and other preparatory processes are equally well suited for dyeing and alternatively can be connected to a dye-impregnating arrangement. It therefore follows that a combination range can be built, which makes it possible to use the equipment for both the dyeing as well as the preparatory treatment depending on operational conditions.

In the bleaching range shown schematically in Figure 4, the impregnating equipment consists of a comparatively small liquor capacity. It is constructed in such a way that the goods are squeezed repeatedly when they pass over the upper guiderolls. In this way excellent penetration is obtained, which is especially important where a wet-in-wet impregnation is concerned. The impregnating pan is completely enclosed in order to prevent tempera-

ture losses when the impregnation is carried out at high temperatures. After the impregnation, the goods run through a pneumatic squeezing arrangement with a maximum pressure of 1500 kg. In preparation processes, however, it is desirable to squeeze the goods only up to 100% so that the maximum pressure is actually used only in exceptional cases.

The infrared zone is not used in the case of impregnating for preparation. Instead there is a short connecting channel made of acid-resistant steel which, like the infrared zone, has a comparatively narrow slot for the fabric. Between the impregnating machinery and the connecting channel, a compensator is arranged in such a way that the tension is kept constant. The entire connecting channel and the slot are electrically heated, so that any condensation on the inside is impossible.

In principle, the construction of the batching chambers used here is the same as in the normal dyeing-in chambers. For this particular purpose, however, a number of additional guiderollers inside the chamber is provided in order to create an additional passageway for heating-up of the fabric. The inside of the chamber is made of highest-quality, acid-resistant steel having 3.5% molybdenum content. The heating elements for the preheating of the chamber, which are evenly spaced across the floor of the chamber, are also made of acid-resistant steel.

The guiderollers have ball bearings with stainless-steel housings and packings. They are made of acid-resistant steel covered with Teflon. Inasmuch as the rollers get in contact with the cold and wet fabrics when they enter, the Teflon covering provides for an additional safeguard against corrosion when chlorite bleaching takes place.

As already mentioned in connection with the dyeing machine, a predetermined wet-bulb temperature is maintained in the chamber. During the preparatory processes, and especially during bleaching, the difference between the wet- and dry-bulb temperatures should be kept a little higher than during the dyeing process to prevent any kind of condensation. If, for instance, the fabric is heated to 90° C, the atmosphere in the chamber is set to 90° C wet temperature while the dry temperature is set for about seven to ten degrees (C) higher. For the heating of the fabric entering the chamber, dry steam is continuously added.

The steam supply is governed by a control valve that is regulated by the wet-temperature thermostat, which is part of the chamber. The wet temperature therefore is kept constant from beginning to end, and the fabric evenly heated to the predetermined wet temperature. The steam in the chamber thus can condense only on the fabric which enters the chamber at a lower temperature, and cannot condense on the inner parts of the chamber which are somewhat overheated.

The chlorine dioxide, which eventually is generated in chlorite bleaching, can only appear in dry gas form, a state in which it does not cause any corrosion.

Thus it can be seen that the Pad-Roll range can be employed most advantageously for a great variety of preparatory processes. Since the speed of impregnation is not dependent on the different reaction times, the range can operate at comparatively high speeds even for processing heavy fabrics for which the treatment in full width is most interesting.

The length of steam passage inside the chamber is amply sufficient to heat up a fabric of 150—200 g/m² from 20 to 90° C, even at a speed of up to 100 m/min. This possibility is especially interesting since treatment in open width is a major problem in the processing of heavier fabrics. If fabrics up to 80 cm are being processed, the production can be doubled by running two pieces side by side provided the goods have a weight of at least 150—200 g/m².

A further advantage is the possibility of alternating between the two processes without waiting for the emptying of the just-filled chamber, as is the case in a stationary range. It is, of course, obvious that, in a stationary chamber with a continuous and simultaneous batching and unbatching of goods, the speed is completely dependent on the weight of the fabric as well as the reaction time.

The bleaching process can be effected with either hydrogen peroxide or sodium chlorite. As the sodium chlorite bleaching may be the bleaching method of the future, it might be of interest here to go into more details.

SODIUM CHLORITE BLEACHING

In bleaching cotton with sodium chlorite, the considerably smaller loss in weight as compared with conventional (chemic bleaching) is most characteristic. This diminishing loss in weight does not, however, mean that the waxes, fats and oils of the cotton are not being removed. The difference in these losses is due to the fact that the bleaching with sodium chlorite leaves the outer layer of a cellulose fiber, which is actually valuable cellulose, unaffected and therefore undamaged.

Contrary to the effects of alkaline treatments and treatments with hypochlorite or peroxide solutions, the cellulose itself is not affected by chlorite bleaching. Waxes and fats are removed by the bleaching process but the cellulose substance itself remains stable so that a well-absorbing fabric results. Tests of comparative absorption for cotton kiered and then bleached with hypochlorite and for cotton bleached with sodium chlorite prove that the wettability of the sodium-chlorite-bleached goods is equal or better, especially if the bleaching with sodium chlorite has been done at a temperature of 90° C or somewhat higher.

It has been found, for instance, that a cotton fabric, which originally contained about 1% ether-soluble waxes, fats and oils, contained about 0.3% after bleaching. If the fabric after chlorite bleaching is treated with sodium carbonate or a slightly alkaline peroxide on a full-width washer, the wax, fat and oil content can be reduced by another 0.1%. Since the outer cellulose layer of the fiber is not affected by the chlorite, the fabric also generally has a better hand when compared with that produced on the other systems.

To summarize, sodium chlorite as a bleaching agent has engaged the interest of the textile industry for two reasons: 1) it is a very mild oxidating agent having no damaging effect on cellulose and regenerated cellulose fibers, and 2) it has a distinctly selective oxidation capacity for the noncellulosic impurities of the fibers, which makes it possible to bleach evenly cotton which contains comparatively heavy motes, provided that suitable operational conditions prevail.

In order to obtain the optimum economic bleaching effect of the chlorite, it is necessary to bleach in a slightly acid medium; which results in the decomposition of the product in two different directions, depending on the fact whether an "acceptor", meaning a substance which easily oxidizes, is present or not. In the presence of such an acceptor the decomposition of sodium chlorite in a slight acid solution will give the following equation:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5\ NaCl + 2H_2O \qquad (I)$$

so that, consequently, four molecules chlordioxide are formed by five mole-

cules of sodium chlorite.

In absence, however, of the acceptor the sodium chlorite gives the following equation:

$$4NaClO_2 + 2HCl \rightarrow 2ClO_2 + NaClO_3 + 3NaCl + H_2O \quad (II)$$

so that only two molecules of chlorine dioxide are formed from four molecules sodium chlorite.

It is evident from these equations that the presence of an acceptor is very important to get the full value of the chlorine dioxide. We know, however, that the chlorine dioxide is not the main bleaching agent of the chlorite but that the chlorite first forms a product, probably chloric acid (which is to be regarded as the interim bleaching agent), which then develops the less reactive chlorine dioxide.

It is therefore important that the chloric acid, which develops from the chlorite, meets the highest possible concentration of an acceptor while it is in the nascent state, so that a reaction which is close to equation I results.

It follows therefore that the best value of the chlorite is much more easily obtained by use of the impregnating process than by bleaching with a high liquor ratio.

It follows further that the danger of corrosion caused by the development of chlorine dioxide would be much smaller when the impregnating system is used.

The speed of the decomposition of the sodium chlorite by acids is proportional to the H-ion concentration and increases with decreasing pH. Further, the speed of decomposition increases with rise in temperature. It is therefore possible to control the dissolution of the sodium chlorite by choosing a suitable temperature and pH value. The object of this control is to have the chloric acid compensated by the "acceptor" immediately without any release of chlorine dioxide, thus not only preventing the loss of the bleaching agent but also avoiding the danger of an increased corrosion factor.

As far as the temperature selected for the bleaching is concerned, it is most practical to keep it at a point no lower than 80° C since, otherwise, the bleaching takes place too slowly. A temperature of about 90° C can be considered as sufficiently favorable provided the setting of the pH value is correct for the impregnating process.

The setting of the pH value of the sodium chlorite bath generally can be effected by the addition of weak organic acids, such as acetic acid, formic acid, lactic acid, etc, or weak inorganic acids, such as the phosphoric

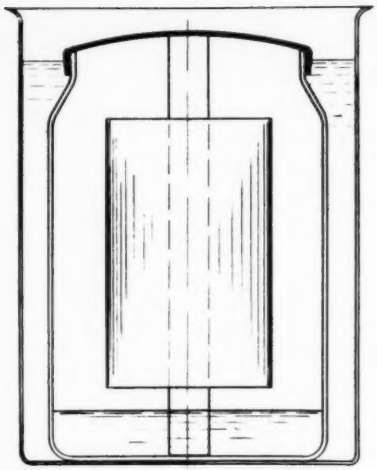

Figure 5

acids. Care has to be taken, however, to ensure that the pH value of the bleaching bath remains constant during the bleaching process. A shifting of the pH value to the alkaline side at the end of the bleaching process could result in a less favorable utilization of the chlorite or too extended bleaching periods.

It is important that the impregnation chlorite bath be kept stable and that the strong feed solution, which serves for supplementation of the impregnating bath, also be kept stable. Concentrations of from 60—100 g/l of sodium chlorite have to be considered normal in these feed solutions in order to meet the conditions created by wet-in-wet impregnation.

The appearance of free chlorine dioxide in the impregnating bath as well as in the feed solution is not only undesirable because of the odor, but also could, under certain conditions, lead to corrosion. Free chlorine dioxide also means a loss of bleaching potency since the chlorine dioxide as such is less potent as a bleaching agent than the sodium chlorite.

It follows that, even if the stability of the bleaching baths in impregnating is of such importance, these have to be activated in such a way that the bleaching agents—most probably the chloric acid—are set completely free if the temperature is increased, say to about 90° C. *This constitutes one of the difficult problems of chlorite bleaching.* It is comparatively easy to achieve a concentrated, stable chlorite solution by setting a pH value of between 5 and 6. It becomes apparent, however, that the acid quantities added in this case are insufficient to activate the whole of the chlorite.

Laboratory trials made with the normal acid-activating methods using formic or acetic acid prove that a proper activating is a fairly difficult problem if all requirements for the process are to be realized. It was therefore obvious that a new way had to be found.

Thus experiments were made with the Pad-Roll method to solve this problem. Starting with a pH of about 6.5-7, success has been achieved in transforming at least 96% of the chlorite at a temperature of 90° C, and very good bleaching effects were obtained within 1-2 hours. Such utilization of the chlorite must be considered to be especially good, and, compared with other activating methods, a considerable saving of chlorite has been made possible. As the chlorite can be utilized to its maximum, and only small amounts of the activating agent are necessary, quite interesting economic aspects are involved.

In order to get a picture of the chlorite bleaching process, it is suggested that the following experiments be made:

1) Four strips of about 2″ width each are taken over the full width of the dry, in-production, desized goods to be bleached. The strips are then impregnated with concentrations of 10, 12, 15 and 20 g/l sodium chlorite and activator (if cotton goods are involved). To the impregnating baths, a chlorite-resistant wetting agent is added (0.5 g/l).

The strips are squeezed with a suitable apparatus at room temperature, keeping the squeezing effect most closely to the squeezing effect used in the actual production machine or about 100%.

After being squeezed, the strips are rolled on glass rods. Special attention must be given to the fact that they should closely and firmly adhere. Finally they are kept together by a thread. The glass rods protrude about ½ to 1 inch.

The rolls so formed are then inserted into bottles with a wide opening, the bottles holding from 200—300 cm^3, being provided with a screw cap, and containing 1—2 cm^3 water. The bottles then are closed and placed in a water bath which has been brought to a temperature of about 95° C. (See Figure 5).

It must be observed whether, and at which concentration of chlorite activator, a green shading occurs. If such a shading occurs only after the bleaching is completed, ie, after one and a half hours, it means that an excessive quanity of chlorite is present. If, however, the green shading occurs very quickly, it is proof that a wrong dose of the activator is being used and the concentration of same

has to be decreased.

In this manner it is possible to determine the quantity of chlorite necessary. The development of a small quantity of chlorite dioxide, meaning a slight green shading, does not constitute any danger since, in the actual production process with the larger quantity involved and due to the fact that the goods are much more compactly rolled up, the free chlorite dioxide will not be noticeable.

It should be pointed out here that the construction of the Pad-Roll bleaching chamber is such that an excess of free chlorite dioxide does not constitute any danger. This is so because the heated walls of the chamber make condensation impossible.

2) The determination of the chlorite, which after the bleaching is still unused and present, can be made by extracting about 10 grams of the bleached goods with 100 cm^3 water, which at normal temperature is poured several times on the goods and squeezed off, and then titrating with thiosulfate after adding potassium iodide and sulfuric acid.

If, after the bleaching process, considerable quantities of unutilized chlorite remain on the fabric, this proves that either the activation was incomplete or the bleaching period or the temperature were insufficient.

These analyses do not take into consideration all the possible factors of the chlorite decomposition. Depending on the selection of the activating agent, the temperatures, the pH values, etc, smaller or larger quantities of hypochlorite or chlorate are generated which are of very little interest for the bleaching. In this presentation, however, it is not necessary to evaluate the nature of these byproducts of the chlorite splitting.

The bleaching with chlorite in bulk must always be done on fabrics carefully desized. The process is as follows:

The grey goods are impregnated first on the impregnating equipment of the Pad-Roll range in a desizing bath, eg, 10 g/l biolase or a similar product, at a temperature of about 60°C, and then heated up in the chamber to about 80° C, batched and kept there for about 20 to 30 minutes after the last end of the fabric has entered the chamber.

The fabric which has been desized in this manner is then carefully rinsed on an open-width washer, heavily squeezed and rolled up on a large-diameter batch. It is most suitable to desize several lots consecutively and rinse these lots (possibly ¼ to ½ of the daily production). The large batches will then be kept in slow rotation until the impregnation for the bleaching can take place. The batches possibly can be covered with a plastic, so that no evaporation occurs.

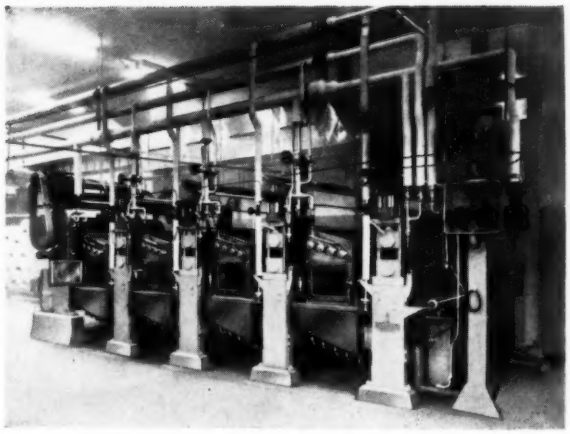

Figure 6
Svetema Open-width Washing Machine

After the desizing of the goods, the bleach impregnation is started and the goods will absorb an additional 20—30% of liquor. The necessary quantity of chlorite most suitable for the fabric to be bleached has been predetermined in the laboratory. If, for instance, 1.5 chlorite per kg is necessary, the bath is set to 15 g/l chlorite, assuming a final squeeze effect of 100%. If the entering fabric contains 75% water, it follows that the feed concentration is 60/l. The impregnating bath will be kept at a temperature below 20° C and then heated in the reaction chamber to about 90°C. The fabric remains in the chamber for a period corresponding to the laboratory tests so that the chlorite is fully utilized. Normally a period of from one to two hours will be required.

After the bleaching, the goods are rinsed again in an open-width washer in order to remove possible residues of acid chlorite, and, if desired, they can be treated in the first compartment of the washer with 2 g/l of hot sodium carbonate. In the next compartment, the goods are rinsed hot and then cold. Possibly, there will be an afterbleaching with an alkaline peroxide solution in two compartments with additional rinsing. The afterbleaching bath can consist of 0.5 cm^3/l hydrogen peroxide 35% and 1-2 g/l sodium carbonate.

The temperature at this point should be 60—70° C, and it might be advisable to add here a suitable detergent.

Figure 6 shows an open-width washing machine which has proven to be extremely efficient and economic in operation and which is recommended in connection with the bleaching range.

This washer works at a comparatively small bath volume on the counterflow system, whereby extremely low water and heat consumption and an excellent washing effect are achieved. The washing effect and the counter-current principle are further increased and their efficiency fully utilized by the comparatively light squeezing against the upper guide rollers, which insures complete penetration. The turbulence, ie, the flow of the water coming from the fabric, which is so important for an efficient washing action of the goods, is further increased by the fact that the passage above the bath level is relatively high.

Since the compartments are completely enclosed, it is possible to operate with boiling baths without any great loss of heat. The desirable and very important tensionless passage of the goods is guaranteed by a patented "relax" drive acting on the upper guide rolls.

ADDENDUM

Since this paper was presented last year, the activating method mentioned has been fully tested in production scale on most different kinds of cotton and rayon fabrics.

The results obtained have been most satisfactory and the essential chemical problems in connection with the chlorite bleaching have been solved. The newly investigated method of activating sodium chlorite calls for the use of an activating agent in a special and (in respect to the most suitable pH) stabilized form, which is distributed by the Svetema organization under the tradename "Activeur PR".

The new method used on a Pad-

Roll machine offers an enormous improvement in chlorite bleaching from the economical point of view as well as from the view that the risks of development of free chlorine dioxide and corrosions are reduced to an absolute minimum.

The most important feature of the activating method is the complete utilization of the bleaching activity of the sodium chlorite. Objective tests in production scale have proved that cotton fabrics with this method will show a far better whiteness and complete removal of the heaviest motes with 0.8—1.3% of sodium chlorite 80% on dry cloth weight, while with earlier-used activating methods 1.5—2.0% of sodium chlorite 80% on dry cloth weight had to be used to reach the best whiteness and complete removal of impurities. The wettability of the fabric also will be excellent with this method.

Normally, 0.2% of Activeur PR will be required independent of the amount of chlorite to be used. The price of the Activeur PR is about the same per lb as for sodium chlorite. Activating costs will not be higher than when activating with acetic or formic acid buffered with sodium pyrophosphate.

The fact that bleaching with sodium chlorite on an average will mean 4% higher weight of the bleached fabric than by any kind of alkaline treatment or bleaching combined with the fact that it gives a better hand to the fabric, etc, suggests that the chemicals will pay for themselves. With the low chemical and labor costs involved with this system the chlorite bleaching really becomes most economical.

By this method, materials made of regenerated cellulose are fully bleached with only 0.2—0.3% of sodium chlorite 80%, calculated on the dry cloth weight. Fabrics sized with gelatine or other water-soluble sizes, which do not interfere with the chlorite, can be bleached directly on the grey goods without foregoing desizing.

The impregnation bath and feed solutions are maintained at pH 7.5—8 by adding the stabilized Activeur PR. They are completely stable for long periods without any smell of chlorine dioxide. With a very pure sodium chlorite, even feed solutions containing up to 100 g/l of chlorite are completely stable for 24 hours or more. Impregnations can be made with a bath temperature of 40—50° C, which means an improved and most level impregnation. In countries with hot climates, this possibility is a great improvement in that the chlorite solutions do not need to be cooled down. The impregnation baths are not corrosive at all.

For the predetermination of the bleaching recipes described above, special laboratory reaction equipment has been developed which in every respect gives exactly the same conditions as in practice, including the momentary heating of the test fabric. The bleaching in practice thus can always be executed in the most economical way and practically without any development of free chlorine dioxide.

To achieve a correct and level pick-up of chlorite in the entire length of a run independent of the total moisture pick-up of the fabric, a system with a variable feed pump for chemicals combined with level, controlled water supply to the bath has been developed.

The Pad-Roll system for bleaching is most versatile in every respect either for big or small production requirements. Compared with bath processes having a continuous batching and unbatching in the reaction chamber, there are obvious features with the *original Pad-Roll system with exchangeable chambers.* The runing speed can be high and is not limited by higher cloth weights and a corresponding diminishing of the yardage on each batch.

Frequent variations of the properties of goods to be bleached in respect to material, width and weight do not cause any loss of time and production due to the necessity of completely emptying a stationary chamber before a new lot can be taken in operation. The most suitable reaction times can be selected for full utilization of the chemicals with any type of goods by any kind of treatment without interfering with the production capacity.

LITERATURE CITED

(1) *Textil-Rundschau,* No. 2, 51-64 (February, 1955).
(2) *SVF Fachorg Textilver,* No. 2, 78-83 (February, 1955); No. 3, 125-34 (March, 1955).
(3) *J Soc Dyers Col* 71, 894-901 (December, 1955).
(4) *Am Dyestuff Reptr* 44, No. 25, P877-81 (December 5, 1955).

Abstracts

(*concluded from page 760*)

blends provide a "wash-and-wear" characteristic to the fabrics, because the resilience of the cotton component is increased to equal that of the Dacron.

The author also refers to Du Pont's Random Tumble pilling tester, which has been found quite useful for predicting pilling.—WHC

Dyeing of Type 42 Orlon Acrylic Fiber

Woodside, G E, *Can Textile J* 74, 63-5, June 14, 1957

With the widespread acceptance of high-bulk yarns of Orlon acrylic fiber it was natural that there should be a demand for a dyed high-bulk yarn which could be used for various types of pattern work in both knitted and woven goods.

The most obvious method of producing such a yarn is to dye it in skein form. Package dyeing is not practical because of the high shrinkage the yarn undergoes at dyeing temperatures. Skein dyeing procedures have been successfully developed and are employed today both in Canada and in the United States. Because of the nature of these yarns it has been necessary in many cases to make some modifications to existing equipment.

Another method of producing a dyed high-bulk yarn is tow dyeing. The tow, after dyeing, is converted into relaxed and unrelaxed slivers which are blended to produce a high-bulk yarn.

The most significant difference between the two yarns is to be seen in their behavior in boiling water. A skein-dyed yarn will exhibit essentially zero shrinkage, while the tow-dyed yarn will exhibit approximately the same shrinkage as is found in natural high-bulk yarns. In addition, the skein-dyed yarn will be a solid color, while the tow-dyed yarn may be a solid color, a blend of dyed with undyed fibers, or a blend of two or more colors.

The author gives details of the present methods of dyeing Orlon tow, and various types of dyeing machines that may be used. He states that the choice of dye class will be governed by the end-use of the yarn, although for the great majority of the work the cationic (Sevron) dyes can be used. For pastel shades disperse dyes may be employed. Acid dyes applied by the cuprous ion technique would be required only in those few cases where exceptional fastness properties were demanded.

Drying temperatures above 212°F are desirable, as better penetration is assured, the length of the dye cycle is reduced, and less dye is required in many cases.

The author also describes several methods by which the tow may be dried.—WHC

Proceedings of the
American Association of Textile Chemists and Colorists

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October 21, 1957

AATCC Research Report———

TEXTILE USERS OF NUCLEAR RADIATION

AATCC COMMITTEE ON NUCLEAR RADIATION

INTRODUCTION

IT is the law of the land that all users of radioisotopes, above the minute amount corresponding to 10 millicuries, must first be licensed by the Atomic Energy Commission in Washington, DC. Our government bases the granting of such licenses primarily on two safety factors: 1) to insure that a potential health hazard is properly safeguarded, and 2) to make absolutely certain that no fissionable material gets into the hands of possible enemies. The commission controls every one of the thousand or more varieties of man-made isotopes, but this does not extend over the naturally occurring active elements, radium and polonium. The health hazard is guarded by making sure the license is granted only to those familiar with the safe handling of such materials and that the customary precautions in shipping and storing are observed. The military hazard is controlled by insisting on a meticulous accounting of the amount of active material received and used, plus a statement of just why it is wanted. These licenses, when granted, become a matter of public record (*1, 2*).

This report was made up largely by skimming through the lists of industrial permits for the past 10 years and culling out those having a textile application. The firms listed therefore represent the leaders in this field, as none can enter it without a permit.

In order to simplify our presentation, all licensees for a similar purpose are grouped together under such separate headings as "Rubberized Textiles," "Coated Fabrics," etc. Furthermore, there is listed, together with the name of the company, its location and the stated purpose for which the specific isotope was requested.

COMMITTEE
K H BARNARD, *chairman*
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A T CLIFFORD
Riegel Development Labs
W V FOX
Fox Chemical Service
F P McKENNA
Inst of Textile Techonology
H A RUTHERFORD
School of Textiles, North Carolina State College
L SHAPIRO
Borden Co
L UPSHUR
Burlington Industries
I S BERSTEIN*
Tracerlabs, Inc
H J WHITE, JR*
Textile Research Inst
*Cooperating nonmembers

A list of those firms using nuclear radiation for solving textile problems has been prepared from the catalogues of licensees published by the Atomic Energy Commission. Data is given on the specific radioisotope employed and for what purposes the permit was granted. As all users must be licensed by law, this report gives a comprehensive, yet somewhat detailed, account of the current state of the art. No doubt we are now standing on the threshold of greater developments in this new field.

TEXTILE USERS

RUBBERIZED TEXTILES——— Numerically, the most frequent application of nuclear radiation in all types of industry, both textile and nontextile, has been for thickness gauges. Out of some 1200 commercial licenses reviewed here, 408 were for beta gauges. If one may include the rubberizing of fabrics as a textile operation, the proportion of thickness gauges over any other type of textile application becomes even more dominant.

Every important rubberizer either has used, or is now licensed to use, strontium 90 for measuring the amount of rubber compound he applies. A list of such firms would include Goodyear, Goodrich, Firestone, U S Rubber, Seiberling, Mohawk, General, Hood, Armstrong, and Saint Clair as well as such specialty-product manufacturers as Boston Woven Hose and the Northampton (Mass) Rubber Thread Co. Some of the larger companies have separate licenses for their different plants and many date back to 1946. The use of beta gauges is obviously a well-established and accepted method of control in the rubberizing of fabrics.

COATED FABRICS———Apparently Du Pont has been using both strontium 90 and ruthenium 106 for checking its coated fabrics at Fairfield, Conn, and the strontium 90 at its Newburgh, NY plant.

A beta gauge will detect instantly any variation in the amount of coating, and if set to traverse the cloth, will detect these differences at any point, even while the fabric is running and without touching it. Being operated electronically, it can be used both to detect and to automatically control the amount coated. Other coaters similarly equipped would include Columbus Coated Fabrics Corp, Columbus, O; Cotan Div, Interchemical Corp Newark, NJ; Wadsworth Div, Interchemical Corp, Winthrop, Me; L E Carpenter Co, Wharton, NJ; Elm Coated Fabric Co, Brooklyn, NY; Joanna-Western Mills Co, Chicago, Ill; Goodall-Sanford, Inc, Reading Mass; Respro Div, General Tire Co, Cranston, RI; and Weymouth Art Leather Co, So Braintree, Mass.

So here again is a textile application where the use of nuclear radiation as a production control is fairly common and satisfactory.

THICKNESS OF TEXTILES——— Still other applications of beta gauges for more strictly textile purposes are noted in Ewald's & Longstreet's work at the Field Crops Research Branch, USDA on measuring the evenness of yarn, sliver & roving (*3*).

It is claimed that the mass variation per unit of length could be determined more accurately by means of a beta gauge than by any other available

thickness tester. Some commercial licensees, such as Slatersville Finishing Div, Slatersville, RI, and Plymouth Cordage Co, Plymouth, Mass, are reported to have been less successful with it in their particular applications. However, F C Huyck & Sons, Renssaeler, NY, advertises its successful use of it, and American Viscose Corp is using it at Fredericksburg, Va, presumably on cellophane.

It should be understood that the beta gauge really measures mass, not thickness. Of course, with the ordinary material of uniform density, thickness will vary with mass. If the textile varies in uniformity from spot to spot, difficulty in using the gauge is bound to occur. However, the mass is changed by the addition of a textile resin, so that it is possible to measure the resin content by this change before and after impregnating, especially if the resin content is over 10%. Water itself changes the mass, so if the concentration of the resin solution is known, the actual amount of resin in the wet-padded fabric can be obtained. If it can be measured, it can be automatically controlled. This offers some exciting possibilities and is currently being investigated by the Research Committee of the Piedmont Section, AATCC.

DYE APPLICATIONS———Let us turn now from thickness measurements to some analytical and research problems where the delicacy, quickness and exactitude of nuclear measurements make them ideal for the purpose.

In the case of dyestuffs, it is possible to tag them with different radioactive isotopes, which have the same chemical characteristics as the inactive elements, but whose radiation is proportional to the amount of dyestuff present. Thus it becomes possible to measure the exact amount of dye upon a single fiber or tell how much of it was left behind in the beaker, ie, measure the efficiency of the dyeing operation. After that, one can follow the actual loss of dye through abrasion, washing, crocking, etc, quantitatively.

As some radiations darken photographic films, it might be possible to photograph the location of the dye in a single fiber. But this application, while alluring, presents some formidable experimental difficulties.

American Cyanamid Co, at Stamford, Conn, has applied for the use of cobalt 60 in its study of metallized wool dyes. Lowell Technological Institute, Lowell, Mass, similarly is interested in using sulfur 35 for polysulfides and sulfur dyeings.

H J White, Textile Research Institute, Princeton, NJ, is the author of several papers on the subject of absorption of different inorganic salts by hair fibers (*4*). He has related it to wool-dyeing techniques and is doing further work on dyes synthesized with radioactive elements and on the dyeing of viscose fibers.

Jett Arthur of the US Dept of Agriculture's Southern Regional Research Laboratory at New Orleans, La, is another skilled operator licensed to use nuclear radiation in his study of cotton dyeing and the chemical modification of cotton.

Finally the Carolina Textile Engraving Co, Charlotte, NC, is licensed to use phosphorus 35 to follow the contamination of color on a multicolor printing machine from one box to the succeeding one.

In all these cases, radiation techniques give a detectable difference long before any change of shade is visible to the eye, and give a quantitative figure on the exact amount of contamination.

DETERGENTS AND SURFACTANTS———Several companies are using radiation techniques in their research study of detergents and surfactants.

Among those licensed are General Aniline & Film Corp at Easton, Pa, for both carbon 14 and sulfur 35 to investigate how carbon black accumulates on textiles during repeated washings, and also to investigate the interaction of surface-active materials on textiles in the presence of ionic chemicals.

Lever Bros, Cambridge, Mass, and California Research Corp, Richmond. Calif, also use labeled detergents and surfactants on cloth.

Radioactive Products, Detroit, Mich, has had published a paper on detergency efficiency based on their licensed use of copper 65, while York Research Laboratories, Stamford, Conn, is using carbon 14 in a new soiling test method.

The absorption of tagged quaternary compounds on textiles is of interest to Armour Research Labs, Chicago, Ill, while Hercules Powder Co, Wilmington, Del, studies the substantivity of its carboxymethylcellulose to cotton during repeated washing cycles. Similarly, L Shapiro of the Borden Co's Chemical Div, Peabody, Mass, has reported on his company's use of carbon 14 as a tag in a study of the retention properties of polyvinylacetate on cloth during laundering.

In all these cases nuclear radiation permits the detection of the activated element even when diluted a million-fold. The analysis is quick and fairly accurate, whereas the older chemical methods of analysis are relatively slow and laborious. Also, with the older methods, concentrations below one part per ten thousand are generally reported as mere traces. Another factor in favor of the newer method is the ease with which the tagged element can be differentiated from contaminating or interfering elements. A chemist can use a nitrogen determination as an indication of the amount of urea-formaldehyde resin present in a finish, but he would be stopped if nitrogen from an organic dye were present. No such difficulty would be present if the nitrogen in the resin were tagged and a quantitative figure for the amount of resin would be available regardless of whether the textile were dyed or not.

In biochemistry a tagged carbon atom can be followed through its normal growth in a plant without stopping the life of the plant by the usual destructive chemical analysis. For example, Glenn Greathouse of the Orlando Research Labs, Orlando, Fla. has followed the changes of tagged glucosides into cellulose in the living plant (*5*). Harris Research Labs, Washington, DC, has studied the biosynthesis of tagged cellulose and similar polysaccharides. Battelle Memorial Institute, Columbus, O, also uses carbon 14 to follow the mechanism of fungicidal action. The Dorch Seed Farm, Scott, Ark, is studying radiation of cotton seeds so that, through gene mutations, possible improvements in cotton may result.

RADIATION OF FIBERS——— Radiation may effect a deterioration of the fiber or act as a catalyst for copolymerization. Johnson & Johnson. New Brunswick, NJ, is interested in the deterioration of cellulose by gamma rays, while the Borden Co, Peabody, Mass, is studying their effect on plastics.

Polymerization without heat is possible with some synthetics. The irradiation of polyethylene is already commercially feasible. Monsanto Chemical Co, at Springfield, Mass, is working on polystyrenes. North Carolina State College, Raleigh, NC, and The Chemstrand Corp, Decatur, Ala. are interested in radiation effects on textile fibers.

The possibility of curing the usual textile resins without heat is intriguing, but the cost of doing it with gamma rays is likely to be prohibitive.

(*Concluded on page P780*)

Convention Notes

Approximately 90% of the exhibit space for the 1957 AATCC Convention had been sold by October 1st, according to a report by Raymond J Carey, chairman of the Publicity Committee.

This year's convention, jointly sponsored by the Northern New England, Rhode Island and Western New England Sections comprising the New England Region, will be held November, 14, 15 and 16 at the Hotel Statler, Boston, Mass.

As this year's Convention will be the only opportunity within the next two years for textile mill men to cover a textile wet-processing exhibit, invitations are being mailed to 15,000 executives and technicians to acquaint them with the value of the products and services the exhibitors will display.

It is still possible to obtain space to reach this important segment of the textile field. Information may be obtained from R R Frey, AATCC Headquarters, P O Box 28, Lowell, Mass.

Among the concerns who have taken space, and who are contributing to one of the most diversified AATCC-sponsored exhibits in many years, are the following:

Alco Oil & Chemical Corp
American Aniline Products, Inc
AATCC
American Society for Testing Materials
Atlas Electric Devices Co
Buschman Products Inc
Celanese Corp of America
The Chemstrand Corp
Ciba Co, Inc
Clark Publishing Co, Inc
Cleworth Publishing Co, Inc
Custom Scientific Instruments, Inc
Diamond Crystal Salt Co
Dow Corning Corp
Elmo International
Fabric Research Laboratories, Inc
Fairchild Publications
The Foxboro Co
Gaston County Dyeing Machine Co
General Electric Co
Goodyear Tire & Rubber Co
Hilton-Davis Chemical Co Div
Howes Publishing Co, Inc
Instron Engineering Corp
Instrument Development Labs, Inc
International Salt Co, Inc
Macbeth Daylighting Corp
McGraw-Hill Publishing Co, Inc
Morton Machine Works, Inc
Morton Salt Co
National Council for Textile Education
Nopco Chemical Co
Nu-Lite Corp
Nuodex Products Co
Olin Mathieson Chem Corp
Onyx Oil & Chemical Co
Rohm & Haas Co
W R C Smith Publishing Co
Tanatex Corp
Testfabrics Inc
Turbo Machine Co
Union Carbide Chemicals Corp
United States Testing Co Inc
Warwick Chemical Co Div
Edwin L Wiegand Co

Complete exhibit descriptions, booth numbers, and personnel in attendance will appear in the November 5th (AATCC Convention) issue of *American Dyestuff Reporter*.

AATCC Calendar

COUNCIL
Nov 14 (Lowell Technological Institute, Lowell, Mass); Jan 24 (New York, NY); May 23 (Philadelphia, Pa); Sept 19, 1958 (Piedmont area)

NATIONAL CONVENTIONS
Nov 14-16, 1957 (Hotel Statler, Boston); Oct 30-Nov 1, 1958 (Hotel Conrad Hilton, Chicago); 1959 (Sheraton Park and Shoreham Hotels, Washington, DC); Oct 6-8, 1960 (Sheraton Hotel, Philadelphia, Pa); September 28-30, 1961 (Buffalo, NY)

DELAWARE VALLEY SECTION
Nov 1 (Kugler's Restaurant, Philadelphia, Pa); Dec 6 (Kugler's Restaurant, Philadelphia, Pa)

HUDSON-MOHAWK SECTION
Nov 22 (Johnstown, NY area); Jan 24 (Albany, NY); Mar 28 (Johnstown, NY area); May 16 (Ladies Night); June 20 (Summer outing)

MID-WEST SECTION
Oct 26, Feb 15 (Hotel Bismarck, Chicago, Ill); April 19 (Netherland Hilton Hotel, Cincinnati, O); June 13-14 (Outing—Browns Lake Resort, Burlington, Wis)

NEW YORK SECTION
Dec 6, Feb 7 (New York, NY); April 11 (New Jersey area)

NIAGARA FRONTIER SECTION
Oct 25 (Joint meeting with CATCC Ontario Section at St Catherines, Ont); Dec 6, Feb 21 (Buffalo); Apr 4 (Joint meeting)

NORTHERN NEW ENGLAND SECTION
Dec 6 (Annual meeting, Hotel Continental, Cambridge, Mass)

RHODE ISLAND SECTION
Oct 24 (Providence Engineering Society, Providence, RI); Dec 5 (Annual Meeting—Johnson's Hummocks Grill, Providence, RI)

SOUTHEASTERN SECTION
Dec 7 (Atlanta Biltmore Hotel, Atlanta, Ga)

WESTERN NEW ENGLAND SECTION
Nov 1 (Annual meeting, Hartford, Conn, area); Dec 13 (Rapp's Restaurant, Shelton, Conn)

Employment Register

(Address replies to AATCC Headquarters, PO Box 28, Lowell, Mass)

57-13

Education: New Bedford Institute of Textiles & Technology, B S, Textile Chemistry.

Experience: 7 years administrative (not in textile field).

Age: 25; married; veteran, USAF; references.

Location desired: Open — anywhere USA.

10-7, 10-21

Membership Applications

SENIOR

George B Dohring—Dyer, Kenyon Piece Dye Works, Inc, Kenyon, RI. Sponsors: J J Hepburn, J W Timperley. (RI).

Robert D Easdon—Supt of printing, Nashua Finishing Co, Nashua, NH. Sponsors: A W Mack, G D Jackson. (NNE).

Charles R Howard—Plant mgr, A D Julliard & Co, New York Mills, NY. Sponsors: A F Gortvai, A W Thomas. (HM).

Paul H Hughson—Sales, dyes and chem, Du Pont Co of Canada, Ltd, Montreal, Que, Canada. Sponsors: J C Mansfield, N J Mohurak.

Robert J Keithley—Plant chem, Callaway Mills Co, Callon Div, LaGrange, Ga. Sponsors: K W Hays, D T Thompson. (S).

Esley O Langerak—Res chem & supv, E I du Pont de Nemours & Co, Inc, Wilmington, Del. Sponsors: J F Laucius, R A Brooks. (DV).

Charles G McClimon, Jr—Dyestuff sales, Verona Dyestuffs, Union, NJ. Sponsors: B Celantano, E G Channon. (S).

Rural E Meadors—Supv, Res Dye Lab, Dan River Mills Inc, Danville, Va. Sponsors: G P Paine, H M Chase. (P).

Lloyd E Parks—Tech sales, Parks & Co, Charlotte, NC. Sponsors: C Nathanson, A Hustwit. (P).

Fred W Rathgeb—Mgr of research, Toms River-Cincinnati Chem Corp, Cincinnati, O. Sponsors: A A Coleman, A T Brainerd. (MW).

Francis W Rhodes—Supt of dyeing, Charlert, Inc, Westerly, RI. Sponsors: A Hustwit, C Nathanson. (RI).

ASSOCIATE

Jorge A Lorentz—Industrial chemist, A J Renner Sia, Brazil.

STUDENT

Marcel Menard—Student, St Hyacinthe Textile School, St Hyacinthe, Que, Canada. Sponsor: G R Boule.

Gaston Plante—Student, St Hyacinthe Textile School, St Hyacinthe, Que, Canada. Sponsor: G R Boule.

Lalande Viateur—Student, St. Hyacinthe Textile School, St Hyacinthe, Que, Canada. Sponsor: G R Boule.

TRANSFER TO SENIOR

Thomas Hatchett—Asst supt, Nathaniel Plant, J P Stevens Co, Dublin, Ga. Sponsors: K D Henry, G W Spicer. (S).

Textile Users of Nuclear Radiation———

(*concluded from page P778*)

OTHER APPLICATIONS——E S Guilfillan, of Manchester, Mass, the author of several papers published in the *Textile Research Journal* on the effect of nuclear radiation on cotton, is licensed to use cobalt 60 or strontium 89 to dissipate static generated by moving machinery.

Another even more fundamental mechanical problem is the movement of textile fibers during drafting and spinning. Individual wool fibers have been labelled with phosphorus 32, and their relative movement in the roving as it was being formed has been followed with two Geiger counters. This and many other new uses for nuclear radiation are discussed in a paper given at the 1957 Spring meeting of the Piedmont Section at Roanoke, Va (*6*).

CONCLUSIONS

About fifty firms mentioned in this report actually are using some form of nuclear radiation in connection with textiles. The majority of those listed are using beta-ray thickness gauges, and the rubberizers of cloth lead all others in this connection. Several dye and chemical companies have done textile research work with this new tool and some of our leading textile schools report success; however, progress to date may be regarded as so much spade work. The full benefits will be harvested only when more general recognition is given to the infinite possibilities in the application of nuclear radiation to textile problems, both in research and in production control.

LITERATURE CITED

(*1*) "Industrial Utilization of Radioisotopes—1946 to 1956", Atomic Industrial Forum, 3 East 54th St, New York 22, NY.
(*2*) "Isotope Licensees—July 1946 to Feb 1956", Division of Civilian Application, U S Atomic Energy Commission, Oak Ridge, Tenn.
(*3*) Ewald and Longstreet, "Uniformity Analysis of Yarns, Rovings and Sliver Using Beta Gauges", USDA Cotton Field Station, Knoxville, Tenn.
(*4*) White, H J, Jr, and Moncrieff-Yeates, M, "The Interaction of Cellulose with Simple Salt Solutions and with Dyebaths", *Am Dyestuff Reptr* **46**, No. 3, P87-96 (Feb 11, 1957).
(*5*) *Science* 117, 553-4 (May 22, 1953).
(*6*) Berstein, Irving A, "Applications of Radioactivity in the Textile Industry", *Am Dyestuff Reptr* **46**, No. 11, P399-404 (June 3, 1957).

AATCC MEMBERS ARE URGED TO NOTIFY THE SECRETARY'S OFFICE OF ANY ADDRESS CHANGE.

Activities of the Local Sections

Mid-West

THE Fall Meeting of the Mid-West Section will be held this Saturday, October 26, at the Bismarck Hotel, Chicago, Ill.

The program will begin at 3 pm with a business meeting highlighted by election of officers for 1958. This will be followed by a paper by B J Simpson, Dow Corning Corp, on the subject, "Silicone Softeners and Their Use in the Textile Industry."

At the evening session, following dinner, George O Linberg, president, George P Paine, executive secretary, and Charles W Dorn, chairman of the Executive Committee on Research, will present a picture of current AATCC operations.

Niagara Frontier

ON September 27, 1957, the Niagara Frontier Section held a meeting at the Buffalo, NY, offices of National Aniline Div, Allied Chemical & Dye Corp.

Chairman W H Leyking opened the meeting by introducing Councilor B K Easton, who asked for opinions on the proposal that National Conventions be held every other year and area conventions be substituted in the intervening years. It was unanimously decided that the Niagara Frontier Section is in favor of these proposals. Mr Leyking also introduced K A Lister, vice chairman of the Section, who reminded the members of the joint meeting to be held with the CATCC's Ontario Section at St Catherines, Ont, Canada, on October 25th.

Speaker of the evening was A Khawan, National Aniline Div, who discussed "Isocyanates—Base Polymers and Their Uses." A brief history of isocyanates was given, and their basic reactions were described with emphasis on the reaction with polyols to form urethanes. Uses of urethanes as rigid and flexible foams, rubbers, coatings, and adhesives were discussed. Samples of these products were displayed.

Light refreshments were served at the close of the evening.

South Central Section

J Fesperman, vice president, Katherine Rug Mills, discussed "The Coming Trends in the Tufted Industry" at the September 20th meeting of the South Central Section. The meeting, held at the Hotel Patten, Chattanooga, Tenn, was followed by the usual banquet. Following this, a group attended the Chattanooga-Jacksonville State football game.

Piedmont

THE Trustees of the Charles H Stone Scholarship Fund of the Piedmont Section have announced the awarding of $250.00 scholarships to Bobby Joel Bailey of Route 4, Box 24, Rutherfordton, N C, a senior at North Carolina State College, majoring in textile chemistry and dyeing; and to James Cecil Hunter of Rte 1, Green Mountain, N C, a junior at Clemson College, majoring in textile chemistry and dyeing.

This is the third year these awards have been made. It is planned to continue these awards annually to a senior or junior majoring in textile chemistry and dyeing at North Carolina State College, Raleigh, N C, and at Clemson College, Clemson, S C.

An earlier announcement to the effect that the directors of the Charles H Stone Scholarship Fund had selected Mr Hunter and William A Mills, III to study under the fund for the 1957-8 academic year [cf *Am Dyestuff Reptr 46*, P709 (Sept 23, 1957)] was in error as regards Mr Mills' selection.

Pacific Southwest

THE 1957 Outing of the Pacific Southwest Section will be held this weekend (Oct 25-27) at the Ojai Valley Country Club, Ojai, Calif. Outing chairman J Raymond Nehmens, E I du Pont de Nemours & Co, Inc, states that all facilities will be available to members and guests, ie, golf, swimming, horseback riding, etc.

The Section held its quartely meeting October 4th at the Gourmet Restaurant, Beverly Hills, Calif. Chairman Melville H Behrendt, Catalina Knitting Mills, Inc, designated the meeting as "Old Timers Night".

News of the Trade

Putnam Chemical Acquires Nova Interests

Putnam Chemical Corp, a corporation formed for the purpose of continuing the business of Nova Chemical Corp on a broader basis, has acquired the business in domestic and imported dyestuffs, pigments, textile auxiliaries, waxes and other related products formerly conducted by Nova. The acquisition took place September 30, 1957.

Nova has served textile, pigment, paper, leather and other industries in the United States and Canada for the past 25 years. Former stockholders of the company have stock interests in Putnam Chemical Corp, which is headed by F G Naumann, president.

Putnam will carry on the distribution in the USA of the dyestuffs, pigments, auxiliaries for the textile and other industries, as well as intermediates and waxes manufactured by Badische Anilin- & Soda-Fabrik AG, Ludwigshafen am Rheim, Germany. These products will be supplemented by those to be produced in Putnam's new plant at Beacon, NY.

Nova's customers will be served without interruption by Putnam from Nova's present location at 153 Waverly Place, New York 14, NY and from the plant at Beacon as soon as completed. The supply of all products and the services heretofore furnished by Nova to its customers both in the United States and Canada will be continued and substantially augmented.

Substantially all of the present management and staff of Nova will continue with the new company. R H Funke will serve as vice president and general manager of the new corporation.

ACKNOWLEDGMENT

WE have been advised of the improper use of the trademark "Viyella", in the article, "Dyeing of Synthetic Fibers—A Dyer's Potpourri" by S G Turnbull, Jr, which appeared in the July 15, 1957 issue of *American Dyestuff Reporter*.

One page 511, reference is made to an "80-20 Viyella-type flannel". It is acknowledged that there is no such thing as a "Viyella-type flannel".

"Viyella" is a registered trademark of William Hollins & Co, Ltd, Nottingham, England.

GAF to Explore Joint Venture With Curtiss-Wright

Announcement has been made jointly by Roy T Hurley, chairman and president of the Curtiss-Wright Corp and John Hilldring, president of General Aniline & Film Corp, that the two companies have entered into negotiations for the purpose of exploring the desirability of a joint venture involving the production and marketing of chemicals basic to the manufacture of synthetic materials, including plastics. If consummated, the joint effort would provide GAF with an outlet for proprietary chemical formulations and Curtiss-Wright with raw materials required in the manufacture of its Curon and other plastic products.

A whole family of materials with a wide range of properties, Curon combines a new concept of thermal and acoustical insulation with light weight and adaptation to decoration. GAF has considerable experience and background in the formulation and production of the basic materials from which Curon and related products are made.

Abstractors Needed by OESDI

Organic Electronic Spectral Data, Inc, Silver Spring, Md, can use a few additional abstractors to help in the completion of the first two-volume set of ultraviolet spectral data.

Mortimer J Kamlet of the U S Naval Ordnance Laboratory, White Oak, Silver Spring, Md, secretary-treasurer of the nonprofit OESDI, said that the abstracting of the spectral data is nearly on schedule in order to meet the publication date of of 1958, with 21,000 spectra already completed. Because of the large number of spectra in recent years, abstractors can be used who can aid English- as well as foreign-language journals.

The final treatment of the spectral data, particularly naming and indexing, will depend on the financial support which the project receives from interested sources. The initial arrangement of the collection is based on molecular formulas and compound names used by authors.

Plans are now under way to assure continuation of the project, which involves the publication of supplementary volumes at regular intervals.

1st Fabulized Licensee

Laughlin Full Fashion Hosiery Mills, Inc, Randleman, NC, is the first company licensed to use the new Fabulized finishing process.

Fabulized, a new finish which is said to give synthetics and blends the highest degree of absorbency yet developed, has just been made available to textile manufacturers by Fabulized, Inc.

In discussing Laughlin's reasons for switching to the Fabulized finish, E W Welborn, Jr, treasurer, pointed out that the use of nylon hosiery is decreasing in spite of the increasing population. Many women object to nylon hosiery because it does not absorb perspiration and feels sticky in the summer and clammy in the winter.

F L Laughlin, president, has stated: "From tests made, we know that Fabulized gives nylon hosiery the absorbency and comfortable feel of silk or cotton, without affecting nylon's important characteristics of sheerness and durability. Fabulized is important because it really does something to nylon. And in providing the missing characteristic of absorbency, the Fabulized finish should stimulate new interest in women's nylons and give the industry a much-needed shot in the arm."

New Venango Southern Representatives

Venango Engineering Co, Inc, Philadelphia, Pa, has named Macon Machine Shop, 2008 Centennial Ave, High Point, NC, as Southern representatives to sell and service Venango rotary dyeing machines, package and rawstock dyeing machines, and other equipment.

CORRECTION

YOUR attention is called to two errors in the advertisement of Moretex Chemical Products, Inc's Moropol 700 on page 45A of the October 7th issue.

It was erroneously stated that the product has a particle size of less than ½ micron. The particle size of Moropol 700 is less than 1/10 micron.

Also, in the paragraph beginning, "The abrasion resistance, durability, servability, and glove-like touch . . .", the word *servability* should be *sewability*.

Package-dyeing Facilities At Dye Masters

Package-dyeing facilities have recently been installed at Dye Masters, Inc, Inglewood, Calif. This is the second such installation to be made in Southern California in the past 5 years.

Nu-Method Moves to New Plant

Nu-Method Dyeing and Processing Corp has announced the removal of its offices and plant to newly equipped and modernized quarters at 128 44th St, Union City, NJ.

New USDA-Clemson Contract

A new research program to study the effects of various synthetic-resin and rubber-latex emulsions upon cotton was announced October 1st by the US Department of Agriculture.

A contract for this research has been negotiated between the Department's Agricultural Research Service and the Clemson Agricultural College School of Textiles at Clemson, SC, where the work will be done.

The contract was negotiated for the Department through its Southern Utilization Research and Development Division at New Orleans, La, as part of a continuing program to develop new uses for cotton and to make cotton fabrics more suitable for present uses.

Many resinous and rubber-latex compounds are now commercially available. Although some of them are already being used to treat cotton, their full possibilities have not yet been explored. In the Clemson study, selected compounds will be used to learn if they will impart desirable new qualities to cotton.

Preliminary analysis shows that some of these compounds can improve cotton's resistance to water, abrasion, weathering, and soiling. Tenting, tarpaulins, and rainwear and other cotton clothing may benefit from such improvement.

James H Langston, professor of textile chemistry and dyeing at Clemson, and Carl Hamalainen of the Cotton Chemical Section at USDA's New Orleans laboratory will direct the research.

Temperature Range of pH Scale Extended

The National Bureau of Standards has extended the temperature range in which pH standards are certified. Formerly the pH scale was determined accurately only between 0° and 60°C; now standard pH samples are available from 0° to 95°C (*1*), an extension made possible by the work of Bower and Bates of the Bureau's physical chemistry laboratories.

The standard pH scale was set up to meet the need for accurate measurement of acidity and basicity in aqueous solutions (*2*). In the manufacture of many commercial products, eg, textiles and dyes, the rapidity and efficiency of the processes depend upon the accuracy with which pH can be controlled. The NBS standard pH scale is defined in terms of several fixed points in much the same manner as is the International Temperature Scale. The primary standards of the pH scale are solutions whose pH values are only slightly affected by dilution or by accidental contamination with traces of acid or alkali from the walls of the container or from the atmosphere. The substances from which the standard solutions are prepared are, in turn, stable materials which may be obtained as certified standard samples from the Bureau.

In order to assign values to the NBS standards, the electromotive force of cells employing the standards as electrolytes was measured. These cells are specially designed, utilizing the highly reproducible hydrogen and silver-silver chloride electrodes. Computation of pH is based upon several reasonable assumed relationships between ionic activities and mean activities. Until recently, data for the standard potential of the silver-silver chloride electrode above 60°C were not available, so in spite of the demands of industry an extension of the pH scale to temperatures beyond 60° was not possible.

A recent determination of the standard potential of the silver-silver chloride electrode included measurements from 0° to 95° C (*3*). With these new data it became possible to assign pH values over the extended range of temperatures to five of the six substances used as standards. The sixth substance recently recommended as a highly alkaline standard (*4*) was not certified for the extended temperature range.

(*1*) Bower, Vincent E, and Bates, Roger G, "Standards for pH Measurement from 60° to 95°C," *J Research NBS* **59**, 261 (Oct 1957) RP 2797.

(*2*) "Standardization of the pH Scale," *NBS Tech News Bull* **31**, 138 (Dec 1947).

(*3*) Bates, Roger G, and Bower, Vincent E, "Standard Potential of the Silver-Silver Chloride Electrode from 0° to 95°C and the Thermodynamic Properties of Dilute Hydrochloric Acid Solutions," *J Research NBS* **53**, 283 (Nov 1954).

(*4*) Bates, Roger G; Bower, Vincent E; and Smith, Edgar R, "Calcium Hydroxide as a Highly Alkaline pH Standard," *ibid* **56**, 305 (June 1956).

GTRC Chemical Div Relocates NY District Office

The New York district offices of the Goodyear Tire & Rubber Company's Chemical Division have been moved to new quarters in the heart of the Manhattan business district at 400 Park Avenue, New York 22.

Sales and technical service for all products marketed by the Goodyear Chemical Division to the textile, rubber, paint, paper, and plastic industries are available through this office.

Personnel affected by the relocation include District Manager D E Neese and field representatives E C Brown, A E Whitney and W T Smith.

New Syl-mer Hang Tags

More than three million items of wearing apparel will bear newly designed hang tags identifying Syl-mer, a silicone finish, during the coming fall-winter season.

The gold, black and white tags in a free-form shape will be seen in retail stores throughout the country to direct consumer attention to the invisible Syl-mer finish, which, it is claimed, makes textiles water-repellent, and wrinkle-, spot- and stain-resistant.

Supplied by Dow Corning Corp, the tags are attached by the manufacturer of the garments made with fabrics that have been Syl-mer finished in accordance with performance standards. Constant supervision of these standards is maintained by a permanent quality control testing program at Dow Corning in cooperation with mill and finisher licensees.

Supporting the tagging drive, Dow Corning has launched a nationwide promotion, lasting from September through December, in which the Syl-mer story will be spear-headed by advertising in leading consumer publications and highlighted in an intensive radio and merchandising campaign in 15 key market areas, in cooperation with participating retail outlets. The modern, free-form style of the tag, modeled after Dow Corning's trade mark, will be used throughout the promotion.

The tag contains informative data on the finish as well as a note on the care of treated fabrics. The tags reportedly were developed to "lend added sales appeal to merchandise at the retail level by pinpointing the extra 'built-in' value given by the Syl-mer finish protection."

Information may be obtained from Dow Corning's Textile Division, Midland, Michigan.

Architect's sketch of the Student Union Building, for which The Philadelphia Textile Institute Foundation is currently engaged in fund-raising drive to obtain $200,000 from the textile industry as partial payment for its erection.

Wool Textile Research To Increase

M J Copley, director of the Western Utilization Research and Development Division of the Agricultural Research Service, U S Department of Agriculture, has announced that funds have been made available by the Congress to expand wool textile processing research. A new laboratory, occupying approximately 12,000 square feet, will be constructed in Albany, Calif, adjacent to the Western Regional Research Laboratory.

The new facility will provide for processing experimental lots of wool on the American worsted system of manufacture from raw wool to finished fabric. It will include equipment for raw wool scouring, drying, carding, gilling, combing, drawing, roving, spinning, twisting, winding, warping, slashing, weaving, piece goods scouring, crabbing, fulling, dyeing, padding, tenter drying, carbonizing, shearing, pressing, and decating.

The expanded research program is an outgrowth of intensive but small-scale studies carried out at the Western Regional Research Laboratory during the past few years. These studies in the chemistry and physical structure of wool fibers served as a basis for improved processing techniques and led to chemical modifications of the fiber to impart new properties.

The new process laboratory will permit larger-scale investigations of product and process development. The results from a more fully rounded program of research will assist the domestic wool industry to keep abreast in the textile race.

The present research staff will be expanded to include, in addition to chemists and physicists, textile engineers and craftsmen. Those interested are urged to write to Harold P Lundgren, head, Protein Section, Western Regional Research Laboratory, U S Department of Agriculture, Albany 10, Calif.

TRI Seminar Schedule

The Fall 1957 Seminar schedule of the Textile Research Institute, Princeton, NJ, began October 10th with a discussion of the structure of animal fibers by John Menkart and Arthur B Coe of TRI.

The seminar presentations will continue through January 23, 1958 as follows:

Oct 24—"Theory of Disperse Dyeing," Howard J White, Jr, TRI.

Nov 21—"Theories of Fatigue Failure in Textiles," W James Lyons, TRI.

Dec 5 — "Transmission of Cotton Fiber Properties," Ludwig Rebenfeld, TRI.

Dec 19 — "Fibers from Ordered Polyolefins," T Waller George, Celanese Corp of America.

Jan 9—"Estimating Parameters in Nonlinear Models," J C Whewell, TRI and Princeton Univ.

Jan 23—"Fractionation of Cellulose Derivatives," Andrew Zalay, TRI.

All seminars will be held at the TRI laboratories, beginning at 2:30 pm. Advance notice of planned attendance to L Rebenfeld, TRI, will be appreciated. The seminars are completely informal and no written reports are prepared.

Master Order Being Made For Standard Test Fabric

A master order is now being made for a standard test fabric that could be used by laboratories engaged in studying the performance of fungicides in soil burial, weathering and other tests.

All interested laboratories are being offered the opportunity to include their needs in this master order. This fabric will be woven and treated according to the specifications approved by representatives from Governmental and industrial laboratories at a meeting held last year at the National Academy of Sciences at Washington, DC.

Since no one organization could use sufficient test fabric to make an individual purchase order commercially feasible, it is planned to have the estimated needs of all the cooperating laboratories for three years manufactured at the same time.

The representatives proposed two types of standard fabric: 1) an untreated cotton duck made to specification, to insure uniformity which would be used for the impregnation of test fungicides; and 2) identical duck treated with 2, 2′ methylenebis (4-chlorophenol), commercially known as G-4. The latter would be used as a reference control fabric in soil-burial tests.

The use of these standard fabrics would provide a means of determining changes in activity of a given soil bed from one test period to another; a means of comparing the effectiveness of fungicides tested at different times; a means of comparing directly the soil beds used by different agencies, and, finally, it would be a means of determining the severity of different weathering periods.

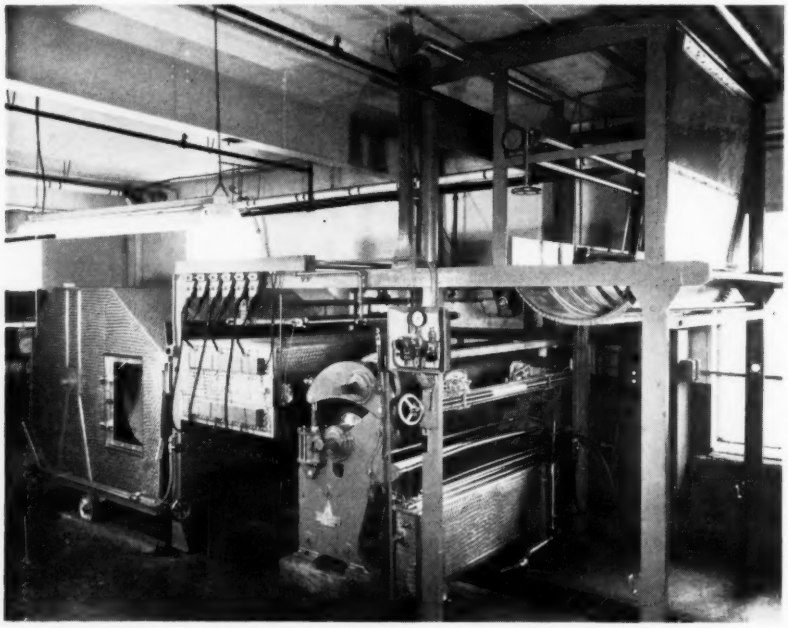
Preparation of uniform 1-inch ravel specimens from these two test fabrics would be facilitated by the use of colored warp yarns so placed that they would outline exactly one inch of the warp. Raveling to these colored yarns would give replicate specimens without the necessity of measuring. When breaking strength determination tests are run after weathering or treatment, any shrinkage or swelling would be automatically taken into consideration since the colored yarns will always outline the same number of warp threads.

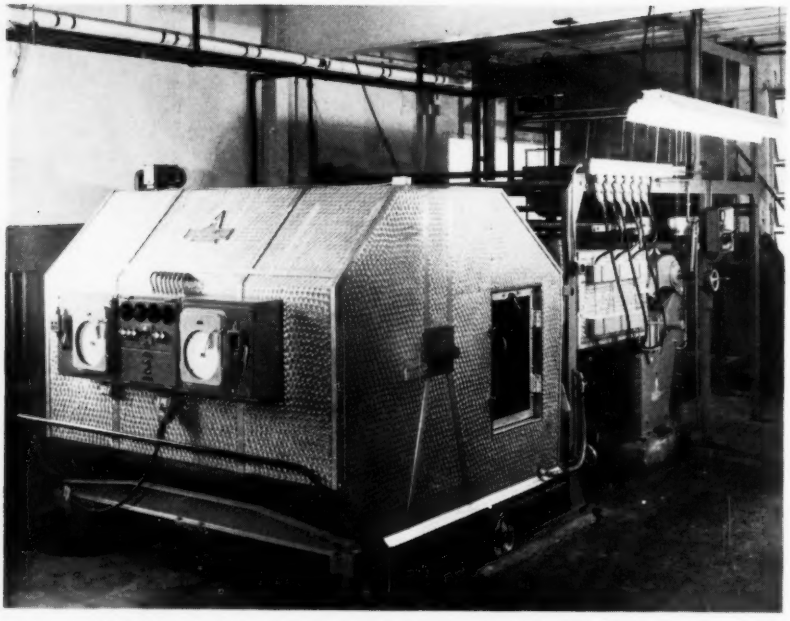
Full information may be obtained from either Samuel Shapiro, Fungus Control Section, Materials Branch, US Army Engineer Research and Development Laboratories, Fort Belvoir, Va, or Patrick J Hannan, Code 6120, Naval Research Laboratory. Washington 25, DC.

New Pad-Roll Installation Lauded

Acceptance of the Svetema Pad-Roll system in the United States has been limited to date, with components of the machinery installed at three textile wet-processing plants in the Northeast. However, enthusiastic response to it bodes well for its future here.

At Northern Dyeing Corp, Washington, N J, where a combination bleaching and dyeing unit was put into commercial operation on August 5th, it has already done a remarkable job.





Two views of the Svetema Pad-Roll Open-Width Bleaching and Dyeing Range in use at Northern Dyeing Corp, Washington, NJ.

The company has been using the equipment chiefly for dyeing. For example, dramatic improvement in the processing of bengalines is expected to enhance Northern Dyeing's already excellent reputation in that particular line. It is acknowledged that, in every instance with the new equipment, the rib of the finished bengaline stands out more clearly and dye penetration is by far superior to that obtained by previously used methods.

Frank J Percarpio, president of the New Jersey firm, which has been noted for its progressive attitude regarding new equipment and methods, has stated that he expects the Pad-Roll system at his plant to be of chief advantage on blends. Robert M Lesh, superintendent, has stated that the system is the nearest thing he has seen to a practical manifestation of Vickerstaff's theories on the physical chemistry of dyeing.

Because of space limitations, Northern Dyeing has improvised somewhat in the use of its portable batching chambers. By using only two chambers, plus an improvised storage area, the company has been able to achieve an operation which for all practical purposes is continuous.

Prompted by reports of the unit, including that given at the 1955 AATCC Convention in Atlantic City, Mr Percarpio last year made a personal inspection of the machinery in three Swedish textile plants. Admittedly looking for an acceptable change from conventional jig dyeing, Mr Percarpio apparently came away convinced that the equipment would be advantageous. The result was that Northern Dyeing, which has spent better than $160,000 this year on new equipment, now boasts the first Svetema machinery fully combining all the dyeing and bleaching units of the equipment.

Technically known as the Svetema Pad-Roll Open-Width Bleaching and Dyeing Range, the unit was manufactured by AB Svenska Textilmaskinfabriken, Gothenburg, Sweden. American representatives for the Swedish firm are Ernest L Frankl Associates, of New York, N Y.

Microfix Process

Ciba Co, Inc research has developed a new, simple dyeing procedure, which, it is claimed, offers a convenient solution to the problem of union dyeing of blends in solid shades, as well as a fast, economical method for dyeing many single-fiber fabrics.

The all-new Microfix process reportedly is being used to dye pale and medium-depth shades of very good fastness on woven and knitted fabrics made from all types of natural and synthetic fibers. It is a short, one-bath pad-dyeing procedure, followed by drying and curing. Microfix dyes are water-insoluble pigments which are applied in conjunction with three synthetic resin binders, Microfix Binders I, II and III.

Microfix dyeings are said to be notable for their very-good-to-excellent lightfastness in pale and very pale shades; their good-to-very-good fastness to washing at the boil, including washes containing chlorine; their good fastness to dry and wet crocking, and their good-to-very-good resistance to drycleaning solvents. The Microfix process reportedly gives level dyeings and insures excellent penetration of heavy fabrics. Microfix-dyed fabrics show less tendency to shrink and a higher resistance to abrasion and thread slippage than undyed fabrics, it is claimed.

Ciba suggests that the Microfix process should prove extremely interesting in the dyeing of mixed fiber fabrics, particularly those containing one or more synthetic fibers. While some natural and synthetic fibers are dyeable together with different types of dyes, in many cases their varying affinities for the same dyes have been a big obstacle to running good unions. It is claimed that popular combinations, such as Dacron/cotton, Dacron/wool, Orlon/wool, Dacron/acetate, etc, now take on new interest because the Microfix process is no respecter of dyeing affinity and yields a level shade on all combinations.

A further advantage of the Microfix process, according to Ciba, is that dyeing can be carried out in conjunction with the finishing operation, for greater economy and production. Most finishing agents, softeners, synthetic resins and the like, are compatible and can be applied in the same bath with the Microfix dyes, it is reported.

Ansul Isocinchomeronic Acid

Isocinchomeronic acid is now offered by Ansul Chemical Co, Marinette, Wis, on a commercial basis. This chemical, which has not been available recently, is suggested as an intermediate in the preparation of dyestuffs, polymers, etc. Its nitrogen ring is said to offer possible increased dye receptivity in polymer applications.

Ansul's isocinchomeronic acid is described as a light tan to yellow powder with a molecular weight of 167.12, a melting point of approximately 236° C (decomposes) and a neutralization equivalent of 83.56 (pure material). Tentative specifications set its purity at 95 percent. It reportedly has no free water, less than 1 percent isocinchomeronic acid monohydrate, and its nonacidic impurities are less than 5 percent.

More information about Ansul isocinchomeronic acid and samples may be obtained by writing Ansul's Market Research and Development Department.

Pyrazol Fast Sky Blue 7GUL

Extraordinarily good fastness for a bright blue direct dye, plus outstanding money value among all the bright greenish blues, are cited by Sandoz, Inc, as major advantages of its Pyrazol Fast Sky Blue 7GUL. The dyestuff is the latest addition to the company's line of Pyrazol Fast Colors.

Other features of the new dye are said to include its perfect reserve of nylon and acetate fibers and the fact that after treatment with UF or UF/-Sandofix does not cause degradation of the lightfastness. Customer leaflet T-7198 describes this color. Additional information may be obtained from any District Office of Sandoz, Inc.

Zelcon C

Zelcon C, a new fabric conditioner, "for companies who wish to formulate better fabric conditioners for home use," has been placed on the market by Du Pont's Dyes and Chemicals Division.

Unlike many existing softeners, goods laundered with Zelcon C tend to maintain their absorbency rather than build up water repellency, it is claimed. The product is said to keep colors brighter and to leave the whites whiter than fabric softeners now on the market. According to Du Pont, it is also a superior antistatic agent, particularly for garments made with synthetic fibers. It reportedly will not interfere with the effectiveness of the detergent on repeated washings.

While a great deal more laboratory work remains to be done, there are indications that Zelcon C has bacteriostatic properties.

New Burling Table

Birch Brothers, Inc, 32 Kent Street, Somerville, Mass, has announced a new, simplified burling table designed to handle approximately 700 yards of fabric continuously.

The machine is floor-mounted and is equipped with an inclined-table-driven draw roll and ball-bearing guide rolls. The fabric travels down the table to the operator and is then folded into a truck. The drive is by a ¾ hp motor through a variable speed unit controlled by a switch connected to a floor-mounted treadle extending the full width of the machine.

Wilstrip

A liquid titanium preparation for controlled stripping of reducible dyes is now available to the textile trade through A L Wilson Chemical Co, Kearny, N J.

Called Wilstrip, the product comes in highly concentrated form for mixing in a solution with ordinary tap water. Its effectiveness and speed are said to be controlled by varying the strength of the solution and applying heat. It reportedly may be used cold for slow-action stripping, or hot for faster results. Wilstrip also can be used to remove an unwanted color from another without injuring the base color, it is claimed.

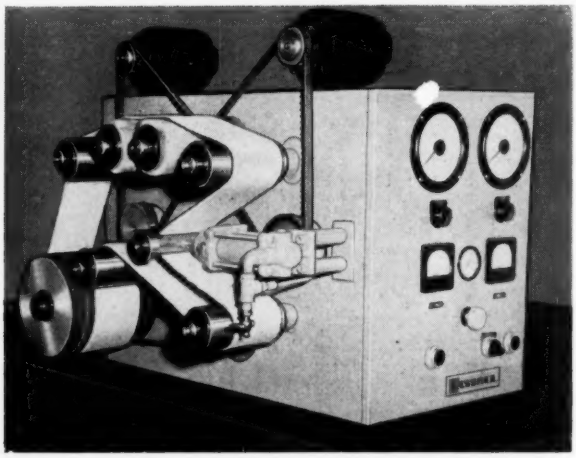
Wilstrip, which is used in the textile maintenance field, is said to have no effect on tensile strength and is suitable for use on cotton, linen, silk, wool and synthetic fabrics.

TMB-5200 Binder

TMB-5200, a newly developed metallic binder for textile printing, which is said to be tarnish-resistant, is currently being manufactured by Kent Printing Ink Corp, Roslyn Heights, N Y.

Bronze and aluminum prints based on TMB-5200 are said to be exceptionally brilliant. No discoloration or loss of brilliance is noted even when the base fabric is scorched under accelerated ironing tests, it is claimed. Competitive products tested under similar conditions reportedly lost brilliance and in some cases scorched severely.

The Company states that prints submitted to Fade-Ometer tests lose no brilliance even after 80 hours of exposure, whereas the best competitive products tested lose brilliance drastically after only 20 hours of exposure. Washfastness and dry-cleaning resistance of the same prints are said to be excellent.



Gessner "Desk Top" Test Napping Machine

"Desk Top" Test Napping Machine

A napping laboratory device in the form of a "desk top", test napping machine has been made available to mills for research and fabric development. This newest product of the David Gessner Co, Worcester, Mass, reportedly simulates, in results, the effects obtained on a Hi-Torc napper. It reportedly permits the study of differences in napping effect on fabrics made of various raw materials, on fabric design, and on fabrics treated with such chemicals as softeners, dyestuffs, etc.

Dial settings are said to be accurate and to indicate the amount of napping power being used, the relative speed between the pile roll and the cloth, the relative speed between the counterpile roll and the cloth, the amount of cloth tension, and the number of napping runs required to produce the desired napping effect.

Research in fabric and fiber development in terms of napping effect is greatly broadened and simplified, it is claimed. It is further claimed that, from quickly interchangeable worker rolls, desired specifications of wire clothing—size, setting and sharpness—can be immediately determined.

Gessner suggests that, as a laboratory device, the machine expands the field of quality control by permitting thorough testing on fabrics already being manufactured.

Houghto-Wax Flake

A change in the physical form of its amorphous wax sizing aid, Houghto-Wax, has been reported by E F Houghton & Co, 303 W Lehigh Ave, Philadelphia 33, Pa.

Composition of the product remains unchanged—a compound of fats and waxes that blends with sizing compound and starch solution. However, it is now being supplied in flake form rather than in solid blocks.

Reasons for the change in the Houghto-Wax product are two, reports Houghton. The flake form speeds "meltability", and is much easier for operators to handle than the older blocks, it is claimed.

A data sheet is available.

Sackner Products Using Pliovic Latex 300 in Auto Door Paneling

Pliovic latex 300 currently is being used in nonwoven binder systems by Sackner Products, Inc, Grand Rapids, Mich in the manufacture of Safoam nonwoven fabrics for use in the automotive industry as door panel padding.

Produced by the Chemical Division of the Goodyear Tire & Rubber Company, Pliovic latex 300 is an aqueous dispersion of vinyl chloride copolymer made at high solids by modern emulsion polymerization techniques. The Goodyear latex is said to be easily compounded to impart adhesion, flexibility and softness to binder systems.

A wide range of physical properties can be made available by varying latex content in binder formulations. Increasing the amount of Pliovic latex 300, for example, gives stiffer hand but increases wet and dry tensile strength.

Sackner utilizes a random web formation in the production of nonwoven fabrics. Through this technique, webs are formed with complete lack of fiber parallelism. Following web formation, the binder is spray-applied to form a smooth, porous and uniform mat ready for drying operations. Chief advantage of random-web-type nonwovens is excellent multidirectional strength.

According to Sackner, Pliovic latex 300 was selected for the application because it exhibits excellent compatability and stability in binder systems, lowers production costs and provides required strength characteristics.

In automobile door paneling, the nonwoven is dielectrically bonded to fiberboard panels to assure a complete and uniform seal and exhibits necessary strength, resilience and dimensional stability for such applications, it is claimed.

Sackner nonwovens are available in widths up to 60 inches and can be colored.

General Calendar

AMERICAN OIL CHEMISTS SOCIETY
Apr 21-23, 1958 (Memphis); Oct 20-22, 1958 (Chicago); Spring, 1959 (New Orleans); Fall, 1959 (Los Angeles)

AMERICAN SOCIETY FOR QUALITY CONTROL—TEXTILE DIVISION
8th Annual Conference—Jan 30-Feb 1, Clemson House, Clemson, SC

AMERICAN SOCIETY FOR TESTING MATERIALS (COMMITTEE D-13)
Mar 18-21 (Spring Meeting, Sheraton Park Hotel, Washington, DC)

THE DRYSALTERS CLUB OF NEW ENGLAND
Oct 25, Jan 20, April 25 (Hotel Vendome, Boston, Mass); June 20 (Outing—Wachusett Country Club, West Boylston, Mass)

THE FIBER SOCIETY
April 30—May 1 (The Clemson House, Clemson, SC)

PHI PSI TEXTILE FRATERNITY
April 24-26 (Annual Convention, Philadelphia, Pa)

SYNTHETIC ORGANIC CHEMICAL MANUFACTURED ASSOCIATION OF THE UNITED STATES
Nov 12 (Palm Terrace Suite, Hotel Roosevelt, New York, NY)

NOV 4 — AATCC CONVENTION ISSUE

DEC 2 — ANNUAL PROCESSING REVIEW NUMBER

• NAMES IN THE NEWS •

Gilbert

Farley

Bowman

Conley

Newcomb

March

Frederick A Gilbert has been named president of the Westvaco Chlor-Alkali Division of Food Machinery and Chemical Corp. Mr Gilbert will continue as president of FMC's Becco Chemical Division.

Franklin Farley, formerly president of Westvaco Chlor-Alkali Division, will again serve as management consultant to the Chemical Divisions. In this new assignment, Mr Farley will be able to apply his extensive managerial experience and skill to all of FMC's broad chemical interests.

Mr Gilbert joined the Becco Chemical Division in 1935. He became president of the Division in 1956. Early this year he was also made a member of the Operating Committee for FMC's Chemical Divisions and moved his headquarters from Buffalo to New York City.

Mr Farley joined FMC as a management consultant in 1954, after serving for many years as vice president of the International Minerals and Chemicals Corp.

Houston

William J Houston has been appointed vice president in charge of marketing of Nuodex Products Co, a division of Heyden Newport Chemical Corp.

Mr Houston, who joined Nuodex in 1946, has been general sales manager of Nuodex since 1955.

William H Bowman has been appointed general manager of American Cynamid Company's Organic Chemicals Division. **Neil B Conley** has been named assistant general manager of the Division, the post formerly held by Mr Bowman. Mr Conley moves up from the post of director of sales and manager of commercial operations for the Division.

The Organic Chemicals Division operates 10 of Cyanamid's more than 40 plants. The Division's seven commercial departments market dyes, textiles resins, pertochemicals, intermediates, rubber chemicals, explosives, and specialty products.

Connell

Richard O Roblin has been named general manager of Cyanamid's newly organized Commercial Development Division, which will have line responsibility for long-range planning, market research, new product development and semiworks production. Dr Roblin moves up from the post of assistant general manager of the Pigments Division, which post has been filled by **Philip G Connell Jr**, formerly manager of the rubber chemicals department of the Organic Chemicals Division.

Independent Chemical Corp, Glendale, NY, has named **Michael Ingber**, formerly with E M Sergeant Pulp & Chemical Co Inc, to its sales organization. He will cover the New York area in his capacity as assistant director of sales.

Gaston County Dyeing Machine Co, Stanley, NC, recently announced the appointment of **Walter J Newcomb** and **Albert P March** as sales engineers.

Mr Newcomb, formerly sales manager of Burlington Engineering Co, heads GCDMC's cloth dyeing machinery division. He is headquartering at the home office in Stanley.

Mr March, who was connected with Smith, Drum Co for many years, will represented Gaston County in the Northeast. He may be contacted at his home in Whitemarsh, Pa. or by telephone in Philadelphia (ADams 3-3580).

Althouse Chemical Co, Division of Crompton & Knowles Corp, Reading, Pa, has announced the addition of **Edwin J Grajeck** to its technical staff, as manager of dye development.

Associated with Collins & Aikman Corp since 1940, Mr Grajeck was manager of research and technical control, as well as technical director for their automotive division.

Carpenter

John M Carpenter has been appointed sales representative for Onyx Oil & Chemical Company's Industrial Division. In his new position, Mr Carpenter will cover the state of Ohio, western Pennsylvania, eastern Michigan, and southwestern New York State, with headquarters at 15017 Detroit Avenue, Cleveland 7, O.

Roberts

William J Roberts has been appointed director of research of the Summit, N J, Research Laboratories of Celanese Corporation of America.

He had been director of research for Pennsylvania Industrial Chemical Corp, Chester, Pa, an organization with which he had been associated for almost 12 years.

In the new function of director of research, Dr Roberts will be responsible for all activities in Summit, site of the Celanese Central Research Laboratories.

Walter F Wigglesworth, formerly with United Piece Dye Works, Los Angeles, Calif, has taken a new position with Calusa Chemical Corp, also of Los Angeles.

George S Barker, formerly with National Automotive Fibres, Inc, Oakland, Calif, and Jenkins-Wright Co, Inc, Los Angeles, Calif, has joined Colorcraft Corp Ltd, San Francisco.

Paul F Noonan, formerly with National Dyeing and Finishing Corp, Culver City, Calif, has joined the staff of Dye Masters, Inc, Inglewood, Calif.

Abbott

Norman J Abbott, formerly with the Textile Department of the Ontario Research Foundation in Toronto, Canada, has recently joined the senior research staff of Fabric Research Laboratories, Inc, Dedham, Mass.

Jimmy L Poteat, a senior in the School of Textiles at North Carolina State College, has been awarded the $360 Union Carbide Chemicals Company Scholarship for the 1957-58 academic year.

Al Underwood has been named West Coast manager of General Dyestuff Co, San Francisco, Calif, to fill the vacancy caused by the recent death of **Robert M True.**

George S Buck, Jr has been assigned to a newly established research post in the National Cotton Council. He will be technical research assistant to Executive Vice President **Wm Rhea Blake,** and will have his headquarters in Memphis.

Establishment of this post is expected to put the Council in a stronger position for expanding cotton's overall research effort. Objective is to provide technical research assistance to the Council's management. Mr Buck, Production and Marketing Director **Claude L Welch,** and Utilization Research Director **Leonard Smith** will constitute a team which will have over-all staff responsibility for technical research planning and development.

TECHNICAL LITERATURE

2,5-DIHYDROXYBENZOQUINONE—*Eastman Chemical Products, Inc, Kingsport, Tenn*—Typical properties and reactions are described for this new Eastman derivative of hydroquinone, which is now available in pilot-plant quantities. Among its suggested applications: polymerization inhibitor, coupling agent, intermediate for dyes, polymers, antioxidants, etc.

LEMOL POLYVINYL ALCOHOLS—(*Bulletin M13-T*), *Borden Co, Chemical Div, 350 Madison Ave, New York 17, NY*—This 23-page bulletin, in three parts, covers "Specifications, Solutions, and Compounding"; "Properties of the Lemols"; and "Industrial Uses of the Lemols".

The Lemols, manufactured by Borden's, "constitute a series of unique water-soluble resins produced by carefully controlled hydrolysis of polyvinyl acetates synthesized to rigidly controlled molecular weights and configurations," the Chemical Division mulletin states.

They are used in the textile industry for finishing, sizing and emulsifying.

SULFONATES—*L Sonneborn Sons, Inc, 300 Fourth Ave, New York 10, NY*—This 12-page booklet describes the origin and manufacture of petroleum sulfonates and details the behavior, functional properties and applications of Sonneborn's line of sulfonates.

Included in the properties and characteristics discussed is information on chemical structure, purity, solubility, stability, viscosity, hard water resistance, surface tension, interfacial tension, wetting and rewetting, spreading, emulsifying and de-emulsifying, and corrosion inhibiting.

In addition, typical tests are shown and end-uses charted.

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